CHEMISTRY
A Textbook for Class XI
Part I

Authors

K. N. Ganesh

V. Krishnan

S. S. Krishnamurthy

M. Nagarajan

B. Prakash

Puran Chand

K. V. Sane

R. D. Shukla

V. N. P. Srivastava

B. Venkataraman

Editors

C. N. R. Rao   K. V. Sane

R. D. Shukla

Chemistry Writing Group

Prof. C. N. R. Rao, F.R.S. *(Chairman)*
Director
Indian Institute of Science
Bangalore

Prof. V. Krishnan
Indian Institute of Science
Bangalore

Prof. K V. Sane
Delhi University
Delhi

Prof. S. S. Krishnamurthy
Indian Institute of Science
Bangalore

Prof. B. Venkataraman
Tata Institute of Fundamental
Research
Bombay

Dr. M. Nagarajan
University of Hyderabad
Hyderabad

Dr K N. Ganesh
National Chemical Laboratory
Pune

Prof. R. D. Shukla *(Coordinator)*
National Council of Educational
Research and Training
New Delhi

Dr V. N. P. Srivastava
National Council of Educational
Research and Training
New Delhi

Dr Puran Chand
National Council of Educational
Research and Training
New Delhi

Dr B. Prakash
National Council of Educational
Research and Training
New Delhi

The National Policy on Education (NPE) 1986 has emphasized the need for qualitative improvement of school education particularly in the area of Science and Mathematics Education. The Government of India has already initiated a number of steps in this direction. The National Council of Educational Research and Training (NCERT) has been assigned the responsibility of developing a new curriculum and related curricular materials in line with the new education policy to serve as a model for the States and the Union Territories to adopt adapt.

The Council set up an Advisory Committee under the chairmanship of Prof. C. N R. Rao, Director, Indian Institute of Science, Bangalore, and Chairman of the Prime Minister's Scientific Advisory Committee, for developing instructional package in science and mathematics from upper primary to senior secondary stage. On the advice of the Committee, different writing teams headed by eminent scientists were formed. At senior secondary level Prof. Rao accepted the invitation of NCERT to work as the chairman of Chemistry Writing Team and to take the responsibility of developing curriculum package in Chemistry. The Chemistry Writing Team consisted of distinguished Chemistry experts from universities, research institutes and NCERT.

The writing team, while developing the present syllabus and the textbook, considered the feedback regarding syllabus and textbooks in vogue. After the textbook was developed, it was exposed to a teachers' workshop to have their comments and suggestions. Suggestions of the teachers were incorporated, wherever possible, before the final manuscript was sent for publication.

I am indeed very thankful to Prof. C. N. R. Rao, who took the leadership of Chemistry team and provided valuable guidance to his team of authors and finally edited the manuscript with Prof. K. V. Sane and Prof. R. D. Shukla. I am grateful to Prof. V. Krishnan, Prof. B. Venkataraman, Prof. K. V. Sane, Prof. S. S. Krishnamurthy, Dr M. Nagarajan, Dr K. N. Ganesh, Prof. R. D. Shukla, Dr V. N. P. Srivastava, Dr Puran Chand, and Dr B. Prakash who authored different parts of the book. My colleagues in the Department of Education in Science and Mathematics, Prof. R. D. Shukla (Coordinator) Dr V. N. P. Srivastava, Dr Puran Chand and Dr B. Prakash took a lot of pains in shaping the manuscript in the pressworthy form and saw it through the press. I am grateful to all of them.

I am very much indebted to the teachers (acknowledged elsewhere) who participated in review workshop and provided valuable suggestions and comments for the improvement of the draft manuscript. I must make a special mention of Prof. A. K. Jalaluddin, Joint Director, NCERT, and Prof. B. Ganguly, Head, Department of Education in Science and Mathematics, who took a lot of interest in this project and extended all possible help in bringing out this book. I also express my thanks to Shri C. N. Rao, Head, Publication Department, and his publication team for making all efforts in bringing out this book in a good form.

Curriculum development is a highly challenging task. No one can claim to have developed a perfect curriculum or curricular materials. Although Prof. C. N. R. Rao and his competent team members did a very good job of writing this book in line with NPE, there can always be some scope for further improvement. I, therefore, request all those who will be using this book to evaluate the materials with an open mind and offer their valuable suggestions, for further improvement.

P.L. MALHOTRA
Director
National Council of Educational
Research and Training

New Delhi
12 July 1988

Preface

'In this introductory book, we have expounded the principles of modern chemistry in the simplest possible language and also illustrated how chemical systems behave and react. More importantly, we have indicated, wherever possible, how chemistry works for man. In presenting chemistry in this manner, we have adopted several strategies. We have given analogies and solved examples; we have also shown how principles come about by describing simple experiments. The strategy has varied with subject matter. We hope to review this book after receiving the reaction from students and teachers to this trial edition. In the meantime, we hope the book will be found useful by students and teachers whose response is of great value to us.

SOLUTIONS TO PROBLEMS: CHEMISTRY

Chemistry deals with the preparation, properties, structure and reactions of material substances. Since diverse substances are present in Nature and in every day life, the scope of chemistry is immense. Chemistry has interfaces with all scientific disciplines and a knowledge of the subject is essential for understanding Nature as well as for the progress of society. A well-trained chemist can not only contribute to the growth of chemical science and industry, but also to other emerging areas of science such as biotechnology and materials science. The future of our society will depend on the availability of such chemists. There is no better way to describe the indispensable role of chemistry than to quote from a lecture delivered by Nobel Laureate George Porter some time ago.

Throughout history, the lot of most of mankind has been rather miserable. Until a few centuries ago it was really slavery and into the last century, although legally free, most men and women had to labour so hard to earn a living that they were effectively slaves to their work. Different professions have had different approaches to this problem. As (Nobel laureate) Max Perutz has put it "The priest persuades the humble people to endure their hard lot, the politician urges them to rebel against it and the scientist thinks of a method that does away with the hard lot altogether".

No branch of science has done more, or promises more, in this respect, than chemistry. It has provided a cornucopia of good things, both of necessities and

luxuries, which have improved our health, and our wealth and also, I believe, our happiness. Man is himself a biochemical system living in a chemical world. His health has been improved out of all recognition by better nutrition, better hygiene and by the drugs which have doubled his lifespan, relieved pain and made it possible for many handicapped people to lead a more normal life.

His wealth, judged in terms of the general availability of the necessities of life, is many times what it was even a few decades ago. This is particularly true of the wealth of food now available in countries which, only a few years ago, were poor to the point of starvation.

Most people today would also class as necessities the plastics, fibres and paints which have made it possible for everybody to be well clothed (though not all may want it!) and to live in a bright, clean environment without having to employ the labour of others to keep it so.

The luxuries, which are also fast becoming universal, often owe as much to chemistry as to the other technologies. This is obvious of such things as motor fuels, cosmetics and dyestuffs but it is also true of electronic devices of every kind, and mechanical, labour-saving appliances. Some of the largest manufacturers of heavy electrical equipment employ more chemists than physicists and, on the newer and lighter side, the silicon *chip* is a highly purified chemical element treated with other elements in a very sophisticated, chemically pure environment.

But perhaps the most successful of all, over the last two or three decades, has been the contribution of chemistry to agriculture. The Green Revolution did exactly what the king of Brobdingnag of *Gulliver's Travels* had asked for and "made two ears of corn or two blades of grass grow where only one grew before" and those who brought it about, according to the king, "would deserve better of mankind and do a more essential service for the country than a whole race of politicians put together". This was a proud achievement of chemistry, depending heavily on fertilizers and new insecticides, plant growth substances and the like. It is a huge industry. The world production of plant food has increased threefold in the last 20 years. India is effectively self-sufficient in food.

We hope that we have succeeded, at least partly, in presenting the flavour of modern chemistry in this book. We look forward to the suggestion of students and teachers for improving the text.

C.N.R. RAO
Chairman
Chemistry Writing Group

National Workshop for Review of Class XI Chemistry Textbook (30 October-3 November 1987)

LIST OF PARTICIPANTS

1. Prof. C. N. R. Rao
   Director
   Indian Institute of Science
   Bangalore

2. Smt. U. Mutreja
   PGT (Chemistry)
   Sardar Patel Vidyalaya
   Lodi Estate
   New Delhi-110003

3. Dr K. N. Upadhyaya
   Chemistry Department
   Ramjas College
   (Delhi University)
   Delhi-110007

4. Shri P K. Sharma
   PGT Chemistry
   Kendriya Vidyalaya
   Lawrence Road
   Delhi

5. Shri P. P. Singh
   Principal
   Bareilly College
   Bareilly (U. P.)

6. Smt. Usha Kiran Jetly
   PGT (Chemistry)
   Kendriya Vidyalaya
   New Mehrauli Road
   New Delhi

7. Dr. V. S. Parmar
   Reader in Chemistry
   University of Delhi
   Delhi-110007

8. Shri C. L. Vermani
   Lecturer in Chemistry
   Govt. Sr. Sec. School
   Banikhet
   P.O. Banikhet
   Distt. Chamba (H. P.)

9. Dr (Smt.) Nayantara Chhetroy
   Lecturer in Chemistry
   Regional College of Education
   Bhubaneswar

10. Dr Rajan Bandiwar
    Master in Chemistry
    Sainik School
    Rewa-486001 (M. P.)

11. Dr J. D. Pandey
    Reader
    Department of Chemistry
    Allahabad University
    Allahabad

12. Shri D. C. Grover
    Lecturer in Chemistry
    SCERT, Sohna Road
    Gurgaon (Haryana)

13 Dr A. K. Kaushal
PGT Chemistry
Army Public School
New Delhi-110010

14 Shri R. D. Saxena
Jr. Science Counsellor
Department of Science Education
SCERT
3, Link Road, Karol Bagh
New Delhi-110005

15. Prof. S. N Mishra
Professor and Head
University of Bhavnagar
Bhavnagar (Gujarat)

16 Prof. H G. Krishnamurty
Department of Chemistry
University of Delhi
Delhi-7

17. Shri Shiv Kumar
Sr. Chemistry teacher
Delhi Public School
Mathura Road, New Delhi

18. Prof K. N. Mehrotra
Department of Chemistry
Agra University, Agra

19 Shri Bhim Sain
Lecturer in Chemistry
Govt College
Jind (Haryana)

20. Dr B. Sharma
Reader
Chemistry Department
University of Gorakhpur
Gorakhpur-273009

21. Shri. M. K. Kulshreshtha
PGT Chemistry
Kendriya Vidyalaya
Mathura Cantt.,Mathura (U. P.)

22. Prof. M. L. Dhar
Department of Chemistry
University of Jammu
Jammu

23 Prof. K. C Joshi
Emeritus Scientist
Chemistry Department
University of Rajasthan
Jaipur-302004

24 Shri S. K. Singhal
PGT (Chemistry)
G. M. Govt. Sr Sec. School
Shahdra
Delhi-32

25. Ms. Shubha Kesavan
PGT Chemistry
Demonstration School
Regional College of Education
Mysore-7

26. Shri R. K. Bali
PGT Chemistry
Nav Hind Girls Sr. Sec. School
New Rohtak Road
New Delhi-110005

27. Prof. B. Venkataraman
Sr. Professor
Tata Institute of Fundamental
Research
Bombay-400005

28. Shri M. Nagrajan
Reader in Chemistry
School of Chemistry
University of Hyderabad
Hyderabad-500 134

29. Shri K. N. Ganesh
Scientist E-II
Organic Chemistry Div. I
National Chemical Laboratory
Pune-411008

30. Prof. S. S Krishnamurthy
    Professor in Chemistry
    Deptt of Inorganic and
    Physical Chemistry
    Indian Institute of Science
    Bangalore-560012

31. Prof. V. Krishnan
    Professor in Chemistry
    Department of Inorganic and
    Physical Chemistry
    Indian Institute of Science
    Bangalore-560012

32. Prof. P. K. Sen
    Professor and Head
    Chemistry Department
    Presidency College
    Calcutta-73

33 Shri K. V. Sane
    Professor in Chemistry
    Delhi University
    Delhi-110007

34. Prof. D. D. Mishra
    Head
    Department of Chemistry
    R. D. University
    Jabalpur
    Jabalpur (M. P.)

35 Dr. Raj Kishore Shukla
    Sr. Lecturer
    Department of Chemistry
    Atarra Post Graduate College
    Atarra-210201, Banda, U P.

36. Shri Ramesh Sharma
    Lecturer (Chemistry)
    State Institute of Science
    Education Punjab
    Chandigarh

37. Dr. R. K. Dewan
    Professor
    Chemistry Department
    Panjab University
    Chandigarh

38. Prof. B. D. Atreya
    MMTC Colony
    New Delhi

NCERT Faculty

1. Prof. R. D. Shukla (Coordinator)
2. Dr V N. P. Srivastava
3. Dr Brahm Parkash
4. Dr Puran Chand

Contents

Unit 10   Redox Reactions

NOTE

Part II of this book for Class XI
will comprise Units 11-19.

UNIT 1

ATOMS MOLECULES STOICHIOMETRIC CALCULATIONS

All things are made of atoms.

OBJECTIVES

In this Unit we shall learn

* to express the result of a measurement to correct significant figures.

* the explanation of the terms: element, compound, mixture; laws of chemical combination; atomic mass; empirical and molecular formula; mole, Avogadro constant,

* to deduce the empirical and molecular formula of a compound;

* to write a balanced chemical equation and use it for various calculations.

THE PRIMARY BASIS of chemistry—like that of all the other sciences is the information obtained through experiments An experiment involves observation of a phenomenon (e.g., melting of a substance, growth of a crystal, reaction between substances) under controlled conditions. The quantitative aspects of a phenomenon (e.g., the temperature at which a substance melts, the rate at which a crystal grows, the amount of energy released/absorbed during a reaction) involve measurement of one or more quantities. All of us are familiar with the measurement of distances, heights, weights, temperatures, etc. in daily life In chemical science, one needs to measure not only these variables but many more like pressure, volume, concentration, density, etc Let us now consider the process of measurement and the manner in which the result of a measurement is expressed.

1 1   MEASUREMENT IN CHEMISTRY

Every measurement *compares* a physical quantity to be measured with some fixed standard, known as the *unit* of measurement. For example, when we say that the width of a page is 8 63 centimetres (usually written as 8 63 cm), we mean that the width is 8 63 times the unit of measurement, which is one centimetre in this case. The width of the page is obtained by using a scale with centimetre and millimetre markings. To express the result of a measurement, two pieces of information are required—the number (8.63) and the unit (centimetre). The measurement of any quantity in science is based on the same procedure.

1.1.1   Significant Figures

When we are dealing with objects which can be counted, we always get an *exact* answer. For example, one can tell *exactly* how much money one is carrying in a purse by counting the notes and the coins. Even when crores of rupees are involved—like in a banking operation—it is always possible to tell the exact amount, down to the paisas. Similarly, when we buy eggs, bananas, chairs, etc. we ask for an exact number and get an exact number. However, try measuring your height with a metre tape or the volume of water in a cup with a measuring cylinder. Though the height of a person or the volume of water in the cup are also *exact* quantities, it is not possible to *measure them exactly.* The difference in the two situations arises because whereas eggs are measured by a discrete variable (there can be five eggs or six eggs but nothing in between), height is measured by a continuous variable (it can be 160 cm, or 161 cm or also anything in between). A scale with centimetre markings can only tell that the height is greater than 160 cm and less than 161 cm. If we take a scale with millimetre markings, it will be possible to measure to the nearest millimetre but not further. In other words, measurement of continuous variable can only be as precise as the choice of the measuring apparatus, but no matter what we do, some uncertainty always remains. Let us see how the uncertainty of measurement is expressed in figures.

The foregoing discussion shows that the result of a measurement may be absolutely precise (as in counting eggs) or it may have some uncertainty (as in measuring a distance) It is useful to include this information in the mode of writing of the result. Scientists have agreed that a number expressing a measurement will include all digits which are certain and a last digit which is uncertain. The total number of digits in the number is called the number of significant figures. In other words, the phrase 'number of significant figures' refers to the precision of a measured quantity, it equals the number of digits written, including the last one, even though its value is uncertain

Consider some examples Suppose the height of a person has been reported in three different ways: 160 cm, 160.0 cm, 160 00 cm. Although the three ways may look equivalent, their scientific significance is different. The number of significant figures in the three cases are three, four, and five respectively which implies the following. In the first case (i.e., 160 cm), the digits 1 and 6 are certain but 0 is uncertain, 0 only represents the best estimate. The usual convention is that the best estimate may be off by ± 1. Thus a reported value of 160 cm means that the true value lies between 159 cm and 161 cm. (Such a result clearly implies that the measurement has been done with a crude scale) The value 160.0 cm has four significant figures. It represents a number which lies between 159.9 cm and 160 1 cm. Note that in this case the third digit 0 is also certain, i.e., the scale used in this case is more precise. The last value similarly indicates that the true number is between 159.99 cm and 160.01 cm, the scale for such a measurement must be even more precise. It is important to realise that the result of any measurement should reflect faithfully the precision of the measurement. To report more significant figures than is possible to measure in a given situation is misleading; to report less significant figures is suppressing some information which can be useful.

The following rules should be observed in counting the number of significant figures in a given measured quantity. (The same rules should naturally be followed when you are expressing the result of any measurement).

1 All digits are significant except zeros at the beginning of the number. Thus 161 cm, 0.161 cm, and 0.0161 cm, all have three significant figures

2. The zeros to the right of the decimal point are significant. 161 cm, 161 0 cm, 161.00 cm, have three, four, and five significant figures respectively

The above rules presuppose that the numbers are expressed in scientific notation In this notation, every number is written as $N \times 10^n$ where

N = a number with a single non-zero digit to the left of the decimal point
n = an integer

For example, 160 cm implies three significant figures but if the measurement is precise to only *two* significant figures, the number should be written as 1.6×10^2.

Scientific notation is also convenient in writing very large and very small numbers. Avogadro's constant (6.022×10^{23} mol^{-1}) and Planck's constant (6.6×10^{-14} Js) will be awkward to write without using the scientific notation

Calculations involving significant figures   To express the result of an experiment, we have to often add, subtract, multiply or divide the numbers obtained in different measurements. It usually happens that these different numbers do not have the same precision Common sense tells that when several numbers of varying precision are combined (i.e., added, subtracted, multiplied, or divided) the final answer cannot be *more* precise than the *least* precise number involved in the calculation. The rules given below should be followed to obtain the proper number of significant figures in any calculation

Rule 1 : In addition and subtraction, the result should be reported to the same number of decimal places as that of the term with the least number of decimal places.

The rule is illustrated by three examples

22 2	4.2042	7.21
+ 2 22	+ 3 1258	12.141
+ 0.222	+ 0.0016	0.0028
Sum = 24 6	Sum = 7.3316	Sum = 19.35

In the first sum, all three numbers have three significant figures but 22.2 has the least number of decimal places, namely 1 The answer is therefore limited to one decimal place In the second sum, all numbers have four decimal places so the answer is also expressed to the same number of decimal places. Note that 0.0016 has only two significant figures whereas the sum has five significant figures. In the third sum, since 7 21 has two decimal places, the answer can have only two decimal places

Similar considerations apply to subtractions as shown by the following examples.

26.382	5.2748	3.74
− 8 4593	− 5 2722	− 0.0016
Diff. = 17.923	Diff.= 0.0026	Diff. = 3.74

In the first difference, the answer is limited to three decimal places whereas in the second one, the answer has four decimal places. Note that in the second example, each of the two numbers have five significant numbers but the difference has only two significant figures. In the last example, 0.0016 has to be neglected since the answer can contain only two decimal places.

Rule 2 · In multiplication and division, the result should be reported to the same number of significant figures as the least precise term in the calculation.

To illustrate the rule, consider the multiplication of 51.028 (five significant figures) by 1.31 (three significant figures). The answer in this case should contain three significant figures, i.e., the same number of significant figures as the least precise term. Therefore 51.028 × 1.31 = 66.8.

In the same manner, if we have to divide 0.18 (two significant figures) by 2.487 (four significant figures), the answer should be expressed to only two significant

figures, i.e, $\frac{0.18}{2.487}$ = 0.072

It should be realized that the basic requirement underlying the two rules is the same, namely, that the result of a numerical calculation should have similar precision as the least precise number involved in the calculation. If in some cases, there arises a doubt about the application of the two rules, it is useful to compare the relative magnitudes of the least precise number and that of the various choices of the result to decide the number of significant figures in the answer. For example, consider again the multiplication 51.028 × 1.31. The relative precision of 1.31 (the least precise number) is one part in 131 or about 8 parts per thousand (usually abbreviated as p.p.t.). The answer should not be written as 66.84, as it implies a much higher precision, namely, one part in 6684 which is about 0.1 p.p.t. If the answer is written as 66.8 the precision is one part in 668, i.e., 1.5, p.p.t., which is similar to the precision of 1.31. Hence we have written the result as 66.8 (Note that in this case writing the result as 66 is not wrong as the relative precision is 15 p.p.t. which is also similar to the precision of 1.31. However, in cases where both answers are admissible, the usual practice is to write the result with the same number of significant figures as the least precise number.)

The presence of exact numbers in an expression does not affect the number of significant figures in the answer. In other words, an exact number is considered to have an infinite number of significant figures. Thus

$$\frac{5.28 \times 0.156 \times 3}{0.0428} = 55.7$$

in accordance with Rule 2.

Rounding off : In each of the examples given above, one obtains more figures than are significant. Thus

$$\frac{5.28 \times 0.156 \times 3}{0.0428} = 55.736075$$

$$= 55.736075$$

In retaining three significant figures, we omitted all numbers following 55.7 because the first number to be dropped (i e 3) was less than 5. However, suppose we had the expression·

$$\frac{5.28 \times 0.156 \times 3}{0.0421} = 56.662803$$

The answer in this case will be written as 56.7 because the first number to be dropped (i e , 6) is greater than 5 This procedure is called ROUNDING OFF It is easily summarised as.

If the figure following the last number to be retained is less than or equal to 5, the last number is left unchanged. However, if the figure is greater than 5, the last number to be retained is increased by one.

1 1 2   SI Units

We are used to expressing distance in kilometres, weight in kilograms, and time in hours In earlier times, many different units were used for the same quantity. For example, distance was expressed in miles, furlongs, feet, etc., weight was measured in pounds, *seers, chataks,* etc It is also common for different professions to employ different units. Thus, jewellers like to use *tolas* and *mashas.* The use of a large number of units causes complications and confusion.

As science became quantitative, scientists found the lack of uniformity to be a nuisance; they also observed that most of the popular systems were cumbersome. (For example, 1 mile = 1760 yards; 1 yard = 3 feet; 1 foot = 12 inches). In 1791, the French Academy of Science devised a simple system, called the metric system, which was soon adopted by scientists throughout the world. As time went by, governments also began to see the advantages of the scientific system and more and more countries began to adopt this system India went 'metric' in 1957. Today, a majority of people all over the world use this system.

The metric system is a decimal system Different units for a physical quantity are related by powers of ten. The different powers are indicated by *prefixes.*   For example, the unit of length is the metre. (Have you heard or seen the 100 metre sprint event in athletics?) A smaller unit is *centi*metre (10^{-2} metre) and a larger unit is *kilo*metre (10^3 metre) Since, 1 metre = 100 centimetres and 1 kilometre ~ 1000 metres, we can do the interconversion by merely moving the decimal place (276 cm = 2 76 m; 2991 m = 2.991 km). Compare this with the effort it takes to convert 276 inches to feet or 1342 yards to miles

Although the metric system was quickly accepted by the scientists, it turned out that a number of different metric units for the same quantity came into use. In October 1960, the General Conference of Weights and Measures adopted a particular choice now known as the International System of Units. It is popularly known as

the SI Units (after the French expression *le System International d' Unit*). The SI Units are now accepted by all scientists everywhere.

The SI has seven basic units (Table 1.1) from which all other units are derived. The standard prefixes, which allow us to reduce or enlarge the basic units, are given in Table 1.2.

The units of mass, length, and time are very familiar since we buy fruits and vegetables in kilograms (or grams), report heights and distances in metres (or kilometres) and measure durations in seconds (or minutes, hours). The unit of

TABLE 1.1

The Seven Basic SI Units

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

TABLE 1.2

The Standard Prefixes for Reducing or Enlarging the Size of any Unit

Multiple	Prefix	Symbol
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

temperature is also familiar through measurement of body temperature during illness or reading of the daily maximum and minimum temperatures in the newspapers. However, we normally use the celsius scale in everyday life (the normal body temperature is 37°C, the maximum temperature on a hot summer day in Delhi is about 40°C and and so on). In the SI Units, temperature is expressed in kelvin (K), a unit named in honour of the great British scientist, Lord Kelvin. The conversion from the celsius scale to the kelvin scale is achieved by adding 273.15 (or less accurately by adding 273) to the temperature on the celsius scale Thus, 0° C corresponds to 273 15 K. The body temperature on the kelvin scale is approximately 310 and a temperature of 300K corresponds to (about) 27°C Note that, by convention, the symbol (°) is not used to indicate temperatures on the kelvin scale

1.1.3 Dimensional Analysis

The seven base quantities lead to a number of derived quantities like area, volume, pressure, force, etc The units for such quantities are easily obtained by defining the derived quantity in terms of the base quantities using the base units. Thus, if the side of a rectangle is expressed in metres (m), the area is expressed in metres^2 (m^2). Similarly, speed (or velocity) is distance/time. So the unit is m/s or ms^{-1}. The unit for acceleration is ms^{-2} and of force (mass × acceleration) is kg ms^{-2}. Some of the common derived units are given in Table 1.3.

It is frequently necessary to convert one set of units to another. The step-by-step procedure for doing this is shown below.

Suppose we want to write 5.0 minutes as seconds (s). We know that

$$1 \text{ min} = 60\text{s}$$
$$\therefore \quad 1 = 60 \text{ s}/1 \text{ min}$$

TABLE 1.3

Some of the Common Derived Units

Quantity	Definition of Quantity	SI Unit
Area	Length square	m^2
Volume	Length cube	m^3
Density	Mass per unit volume	kg/m^3
Speed	Distance travelled per unit time	m/s
Acceleration	Speed changed per unit time	m/s^2
Force	Mass times acceleration of object	kg m/s^2(=newton, N)
Pressure	Force per unit area	kg/(m.s^2) (=pascal, Pa)
Energy	Force times distance travelled	kg m^2/s^2(=joule, J)

Note that the left hand side is a dimensionless quantity since on the right hand side, time is divided by time. Now,

$$5.0 \text{ min} = 5.0 \text{ min} \times 1 = 5.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 300 \text{ s}$$

The advantage of writing the units explicitly is clearly seen. The unit minutes cancel in the numerator and denominator leaving behind unit seconds. If we had written the conversion factor incorrectly, e.g.,

$$5.0 \text{ min} = 5.0 \text{ min} \times 1 = 5.0 \text{ min} \times \frac{1 \text{ min}}{60 \text{ s}} = \frac{1 \text{ min}}{12 \text{ s}}$$

the mistake would have been spotted immediately. You are advised to write units and unit conversion factors explicitly so that mistakes are avoided

Many quantities like force, pressure, energy, etc. are commonly defined in terms of their own units, which are expressible in terms of the base units. It is important to become familiar with these units. It is also important to develop an idea of their magnitude just as we understand how much distance 1 km implies or how much time interval is signified by 1 h

Force: The SI unit of force is the newton ($1N = 1 \text{ kg ms}^{-2}$). To appreciate the size of the unit, imagine holding a mass of 1 kg (about five average sized apples). The force required to hold this is about 10N, since if 1 kg is released, it will fall downwards with an acceleration of 9.8 ms^{-2} or a force of 9.8 kg ms^{-2} (= 9.8N). In other words, 1N is the force needed to hold about 100 g of mass

Pressure: The SI unit is pascal defined as a force of 1N applied to an area of 1 m^2 A popular unit is atmosphere (atm); 1 atm is equal to 101.325 kPa. For rough estimates, we can take 1 atm ≈ 10^{5}N m^{-2}. To appreciate the size of this unit, recall that a 760 mm high mercury column exerts a pressure of 1 atm.

Energy The joule (1 J= 1 Nm) is the SI unit for energy. It is defined as the energy needed to push against a force of 1N through 1 m. If we raise 1 kg of mass by 1 m, we are roughly spending 10 J of energy. Older literature of chemistry quoted energies in kcal mol^{-1} (i.e., kilocalories per mole). The data is easily converted into kJ mol^{-1} by multiplying by 4.184.

1.2 CHEMICAL CLASSIFICATION OF MATTER

It is a remarkable fact that the entire universe is made of only two types of entities —matter and energy. Matter is easy to recognise as it occupies space and has mass. Any number of examples can be given (e.g., house, trees, animals, etc.) since we are

surrounded by material object The idea of energy is more subtle but we can experience the effects of energy just as easily as we can see matter. Light and heat are two of the many forms of energy which are familiar to everyone

Different kinds of matter are made up of substances. Chemistry is that branch of science which investigates the composition and structure of substances. Under certain conditions, substances undergo a change in composition This is called a chemical reaction. The study of reactions is another important part of chemistry

Materials found in nature are either single substances or they consist of two or more substances. A sample containing only one substance is called a pure substance Samples having more than one substance are not pure, they are usually called mixtures. Pure substances are of two types—elements and compounds Mixtures are also of two types—homogeneous and heterogeneous Heterogeneous mixtures are those where the constituents can be seen whereas in homogeneous mixtures, the constituents are so well mixed that the constituents cannot be seen even under a microscope and the sample has uniform composition
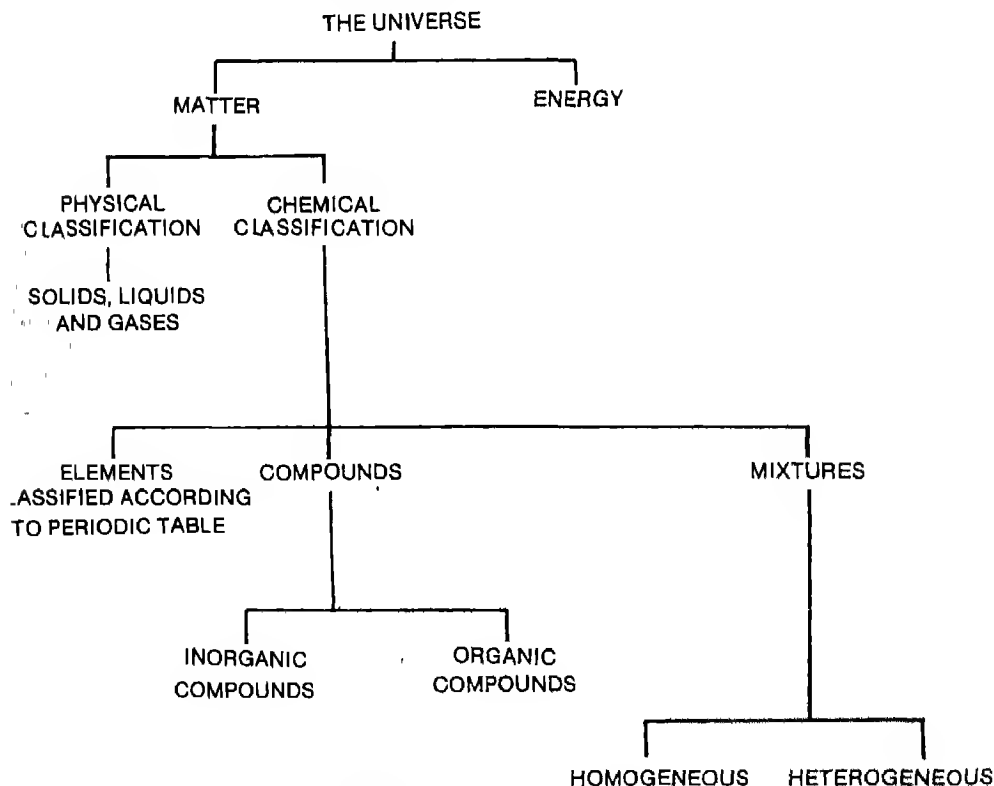
THE UNIVERSE

MATTER   ENERGY

PHYSICAL   CHEMICAL
CLASSIFICATION   CLASSIFICATION

SOLIDS, LIQUIDS
AND GASES

ELEMENTS   COMPOUNDS   MIXTURES
CLASSIFIED ACCORDING
TO PERIODIC TABLE

INORGANIC   ORGANIC
COMPOUNDS   COMPOUNDS

HOMOGENEOUS   HETEROGENEOUS

Fig 1.1   *Classification of matter*

This description is summarised in Fig. 1.1 It is the basis of the chemical classification of matter Another system of classification useful in chemistry separates matter into: (i) gases, (ii) liquids, and (iii) solids. It will be discussed in Unit 2

1.2.1 Mixtures, Compounds and Elements

To grasp the various terms introduced so far, we need to understand better what is meant by a substance. A substance can be identified by its properties. Thus every substance has a set of characteristic properties which distinguishes it from every other substance. Some of the common properties are melting point, boiling point, solubility, colour, and odour. For example, pure water is found to freeze at 273 K and boil at 373 K at one atmospheric pressure; the melting point and boiling point characterise water since there is no other substance with identical values. Similarly, hydrogen sulphide is recognised by its unpleasant smell, and copper sulphate by its beautiful blue colour. Properties of this type are called physical properties since in determination of such properties either the state of the substance does not change at all or only its physical state changes (e.g., water from solid form changes to liquid form during melting). A substance also exhibits another type of property called chemical property, in which the substance undergoes a change in its composition. Some examples are: sugar chars on heating, water decomposes on passage of current, iron rusts. To summarise, *every substance possesses characteristic physical and chemical properties which identify the substance and help us to distinguish one substance from ... . .*

Most of the materials which we commonly encounter are not pure substances but mixtures. Soil, stone, wood, air, water, milk, kerosene, etc., are all mixtures, i.e. they contain more than one substance. Properties of a mixture are dependent on the nature and the amount of the constituents. You can perform a simple experiment with water to understand this fact.

Experiment· Taste a sample of tap water. Taste the sample again after boiling it for a few minutes. Notice the 'flat' taste of boiled water. On adding sugar or salt, the solution will taste sweet or salty. Further, the extent of sweetness or saltiness will depend on the amount of sugar/salt added to water. We conclude that the properties of a mixture are governed by its constituents and that the properties are varied because the composition (i.e., the relative amount of the constituents) of a mixture can be varied.

A salt solution is an example of a homogeneous solution because although the composition can be varied the composition of a given sample is uniform. (Drops of such a solution, taken from different parts, will taste the same.) Another point to note is that we cannot see the salt in the solution with the naked eye or even under

a microscope Homogeneous solutions occur in solid and gaseous states also The gold used for making jewellery is a solid solution of gold with copper or silver while air is a gaseous solution

The constituents of a heterogeneous mixture are not distributed uniformly The properties and the composition of such mixtures are therefore non uniform In some mixtures like concrete, the different constituents like sand and cement can be seen with the naked eye However, though milk seems homogeneous it is actually a heterogeneous mixture Under a microscope, small droplets of fat can be seen to be suspended in a clear liquid. '

Separation of a mixture. How do we know that a given sample is a mixture or a pure substance? If we boil a salt solution, it will be observed that the boiling temperature will not remain constant. This happens because as water evaporates, the composition of the mixture changes and hence its boiling temperature also changes. However, if a sample of pure water is boiled, the boiling point remains constant because evaporation of water causes no change in the composition of the liquid left behind. This shows that any of the characteristic properties of a substance can be used to establish whether the substance is pure or not. If a substance is not pure, how can it be purified? (i.e., how can a mixture be separated?) Once again the
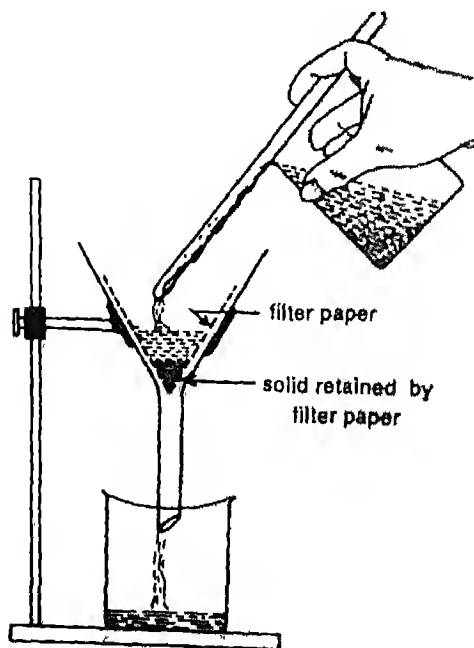

Fig. 1.2(a) *Filtration*

characteristic properties provide the clue. In a salt solution, the boiling points
water and salt are very different. The water can therefore be either boiled off
distilled leaving the salt behind. Similarly, a mixture of salt and pepper can
separated by utilising the fact that salt is soluble in water whereas pepper is n
Dissolution of the mixture in water followed by filtration will yield pepper on t
filter paper and salt solution in the beaker. This salt can be recovered by boili
away the water. In this case, we have used the difference in solubility to effect t
separation

Separation (i.e., purification) is an important operation in chemistry. Eve
chemist who uses materials in the natural form has to employ one or more separati
method to purify the materials. Since no two substances have all properties identic
some method can always be devised which takes advantage of the difference in c
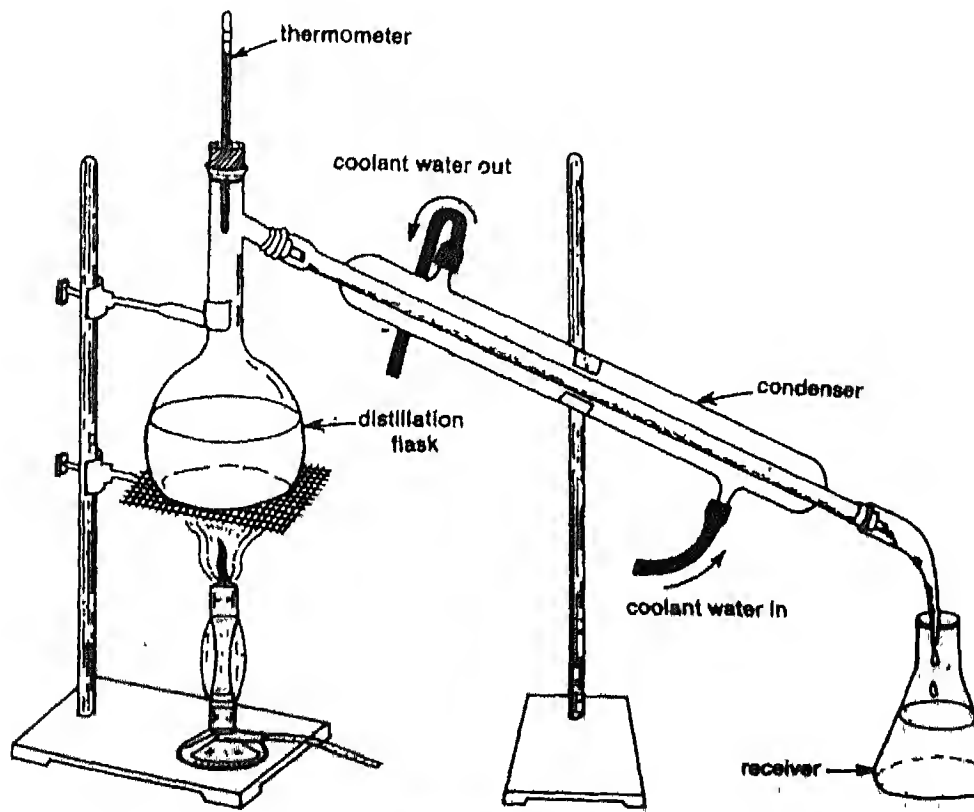particular property. The examples given above used filtration (based on the differer

Fig. 1.2(b) *Distillation*

14

in solubility) and distillation (based on the difference in boiling points) which are the more common methods for separation of a mixture Some other common methods are:

Fractional Distillation· Simple distillation, described earlier, is useful when the boiling points are far apart. When the components of a mixture boil within a narrow range of temperature the technique of fractional distillation is employed Crude petroleum is separated by this technique into different fractions like gasoline, lubricating oil, kerosene, diesel, etc.

Extraction: Water can be used to extract salt from a mixture of salt and pepper because salt is soluble but pepper is not When we make coffee or tea, water extracts the flavour from coffee beans/tea leaves. Similarly, alcohol is used to extract vanillin (vanilla flavour) from vanilla beans.

Gravity Separation· Differences in density is the basis of this method. Wheat harvesting (the light chaff is blown away leaving behind the denser wheat grains), detergent action (soap bubbles surround the dirt on skin/clothes and float them away), and panning of gold (high density gold grains settle at the bottom) are some common examples.
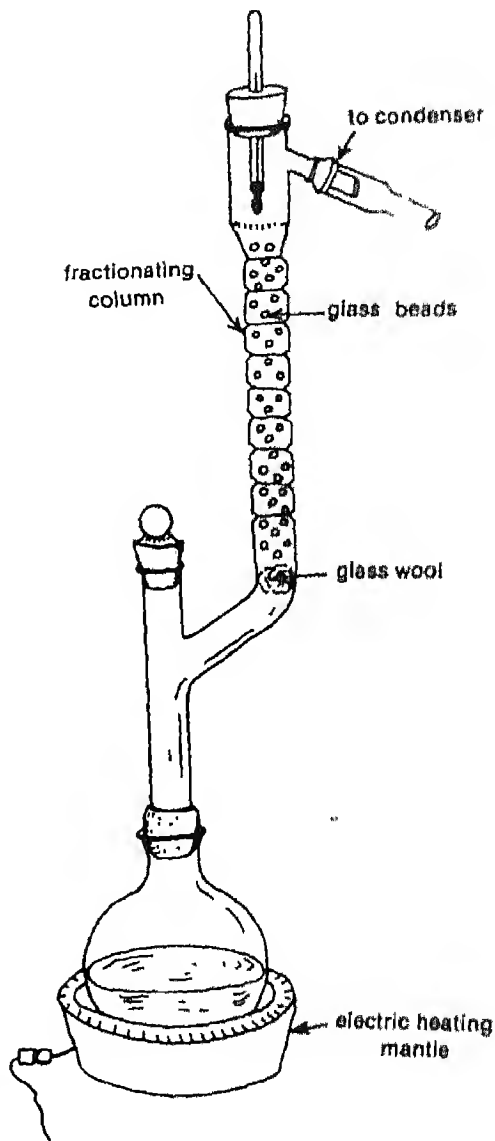
to condenser

fractionating column

glass beads

glass wool

electric heating mantle

Fig. 1.2(c)   *Fractional Distillation*

Magnetic Separation Since iron ore is magnetic, it is separated from non-magnetic waste material by using a magnetic field.

In addition to the above methods, a large number of other methods are also used. Some of these are. chromatography (difference in distribution between a stationary and a moving phase, details in Unit 18), electrophoresis (difference in electrical mobility), ultracentrifugation (difference in sedimentation velocity in a centrifugal field), countercurrent distribution (difference in distribution between two immiscible liquid phase) You will study these methods in advanced classes.
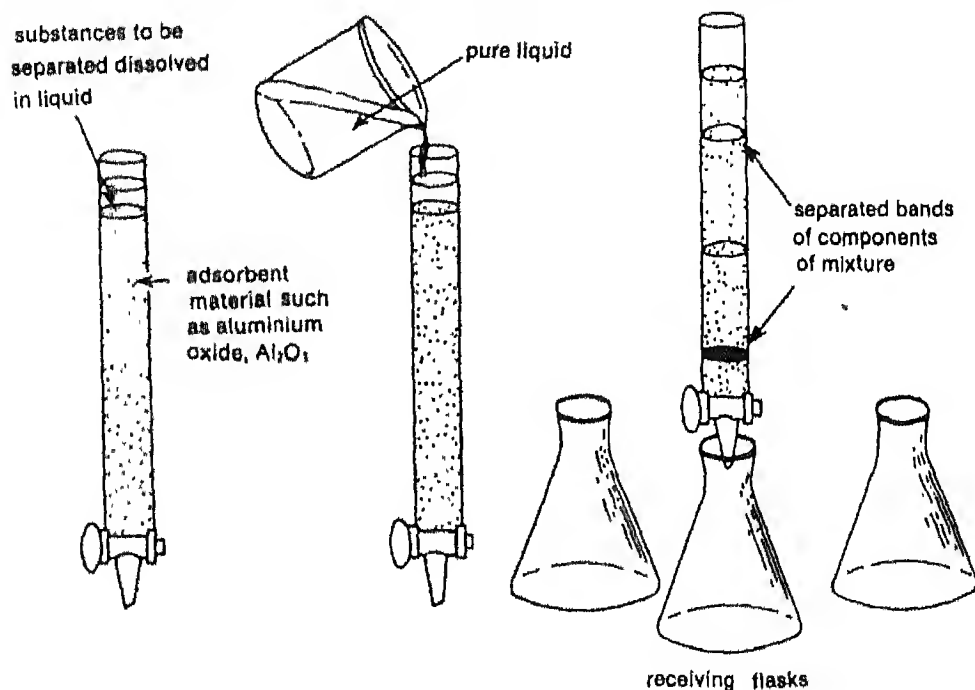

Fig. 1.2(d) *Chromatography*

Elements and Compounds: Once a pure substance has been isolated, the question how to decide whether it is an element or a compound arises. This question proved very baffling in the history of chemistry; the inability to answer it delayed the birth of chemical science until the latter part of the eighteenth century.

The breakthrough was made by the great French chemist Antoine Lavoisier who is rightly regarded as the Father of Chemistry. Lavoisier showed how weighing of substances before and after a chemical change can become a powerful method of understanding many chemical phenomena which had been baffling until then

## ANTOINE LAVOISIER (1743-1794)

Antoine Laurent Lavoisier is generally regarded as the Father of Chemistry. The son of a wealthy French lawyer, Antoine graduated in law but chemistry fascinated him Lavoisier devoted his entire life to the study of a variety of chemical phenomena He was perhaps the first leading chemist to appreciate the importance of quantitative measurements. He arrived at the law of conservation of mass by careful weighing of reactants and products in a chemical reaction. Lavoisier was intrigued by the phenomenon of combustion and he made many discoveries which explained the nature of combustion. Lavoisier established that air consists of oxygen (supporter of combustion) and nitrogen (non-supporter of combustion). This great son of France was ironically a victim of the French Revolution during which he was arrested and guillotined. The famous mathematical physicist M. Laplace who was a contemporary of Lavoisier commented, "It took a minute to behead Lavoisier but it will take thousands of years to make a head like that."

To understand Lavoisier's reasoning, consider the following reaction which is easily studied in the laboratory

$$\text{mercuric oxide} = \text{mercury.} + \text{oxygen}$$
$$\quad\quad 100g \quad\quad\quad 92.6g \quad\quad 7.4g$$
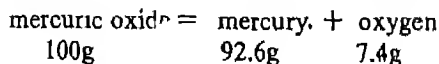
It is observed that mercury (a silver white liquid metal) on heating in air is converted to red mercuric oxide. If mercuric oxide is heated more strongly, it is converted back to mercury. The measured weights show that the weight of mercury is *less* than the weight of mercuric oxide. This implies that mercuric oxide is a compound since it can be broken down into something simpler. It should be

understood that the weight of a substance is being used as a criterion of simplicity. If the weight of a substance decreases because of a chemical reaction, then the reaction has caused a break-up of the original substance. The original substance must therefore be a compound.

However, the above reaction cannot decide the nature of either mercury or of oxygen. If some reaction can be carried out with mercury so that the weight of the product(s) is less than the weight of mercury, then reaction has succeeded in breaking up mercury, and mercury will also be regarded as a compound. However, no one has reported any such reaction so far. The inability to break up mercury further indicates that mercury is an element.

It is natural to question this way of deciding whether a substance is an element or not. Just because no reaction has been found until now which can disintegrate mercury does not mean that such a reaction cannot be found later. If someone is able to perform such a reaction in future, will it not disprove the statement that mercury is an element? This objection is certainly valid. In fact, in the early development of chemistry, there were many instances when a substance thought to be an element turned out to be a compound because a reaction was discovered which could break it up. For example, water was classified as an element until Sir Humphrey Davy succeeded in decomposing it by the passage of an electric current. Similarly, lime was regarded as an element until it was observed that it breaks down in a high temperature electric furnace. It is true, therefore, that such an approach cannot decide with complete certainty that a substance is an element. However, an alternate approach has become possible with the development of the atomic theory to be discussed later in this Unit. For the present, it may be stated that an element is now defined as containing only one kind of atoms and a compound is substance containing more than one kind of atoms. It is possible to use this criterion in an unambiguous way. All the pure substances can thus be classified into elements and compounds and there is no doubt now which substance is an element and which is a compound.

It is a remarkable fact that the entire universe is made from about 100 elements only. Of these 92 are found in nature and the rest are man-made. The elements serve as the building-blocks of all matter. The enormous variety which we see around us arises because elements combine in many ways to form different compounds. The situation is like in a language. For example, English has an alphabet of only 26 letters which are the building-blocks of the language. However, an endless number of words can be formed by combining the letters. Just as the vowels a, e, i, o, u, occur more frequently than the consonants, some elements like carbon, oxygen, nitrogen, hydrogen, form more compounds than the other elements. Indeed, compounds of carbon are such a large and special class, that an entire branch of chemistry, called organic chemistry, is devoted to the study of carbon compounds.

HOW IMPORTANT IS THE DISCOVERY OF ATOMS ?

Professor Richard Feynman, the Nobel Prize winner from U.S.A., has
said:

> If, in some cataclysm, all of scientific knowledge were to be destroyed
> and only one sentence passed on to the next generation of creatures,
> what statement would contain the most information in the fewest
> words? I believe it is the atomic hypothesis...that all things are made
> of atoms... In that one sentence...there is an enormous amount of
> information about the world if just a little imagination and thinking
> are applied.

1.3   LAWS OF CHEMICAL COMBINATION AND DALTON'S ATOMIC THEORY

Reactions are the essence of chemistry. Extraction of metals, refining of oils,
preparation of drugs, are all dependent on the chemist's ability to carry out different
types of chemical reactions. The study of reactions is one of the important areas of
chemistry. There are many aspects to a reaction like the rate of reaction, energy
absorbed/evolved during a reaction, mechanism of a reaction, etc. These topics will
be discussed in different Units. In this section, we will look at the weight and
volume relationships in a chemical reaction. From a historical point, this topic was
of the greatest importance since it led to the formulation of our present concept of
atoms and molecules. .

The atomic theory of matter is difficult to grasp because atoms cannot be seen.
The existence of atoms is inferred by reasoning. Many of the arguments are subtle;
understanding them therefore requires a lot of effort. However, since all modern
science is based on the atomic concept, it is important that every attempt should be
made to grasp this concept as thoroughly as possible. It is interesting to note that
whereas physics and biology made a fair progress without knowledge of atoms,
chemistry could not even begin until the atomic hypothesis was formulated. The
laws of chemical combination are important because they provided the first scientific
evidence for the existence of atoms.

1 3.1   A Simple Analogy

Because the atom is such an   abstract idea, it will be useful if we begin by

analysing a problem where we can see, handle, and weigh objects. The reasoning that we develop can be transferred to chemical phenomena even though we cannot see, handle, or weigh individual atoms.

JOHN DALTON (1766-1844)

John Dalton, the son of a poor weaver, was born in Cumberland, England. He began his lifelong career as a teacher at a village school when he was only twelve. Seven years later he became a school principal. In 1793 he left for Manchester, to teach mathematics, physics and chemistry at a college. He soon resigned from this post since teaching duties interfered with his scientific studies. Dalton never married. He lived a very simple and modest life even after he became famous. From his early years to his death, Dalton carefully recorded the meteoric data each day; temperature, pressure, time, amount of rainfall and so forth. Dalton suffered from protanopia, an inability to see red at all. Much to his amusement this sight defect became known as 'daltonism'.

Dalton put forward the atomic theory in 1803. He proposed that compounds were formed by the combination of atoms of different elements in small, whole number ratios, but had no certain method for determining the ratios in which the different atoms combine. When only one compound of two elements A and B was known, he assumed that it had the simplest possible formula, AB. For example, he assumed that the formula of water is OH. He deduced relative atomic masses, on the basis of this type of assumptions. He was the first to publish a table of relative atomic masses. Since his assumptions about formulas of compound were not always correct, there were errors in his table which were corrected only in 1858. Nevertheless, the credit must go to Dalton for first putting the atomic theory on a quantitative basis and for laying the foundation for the rapid development of chemistry.

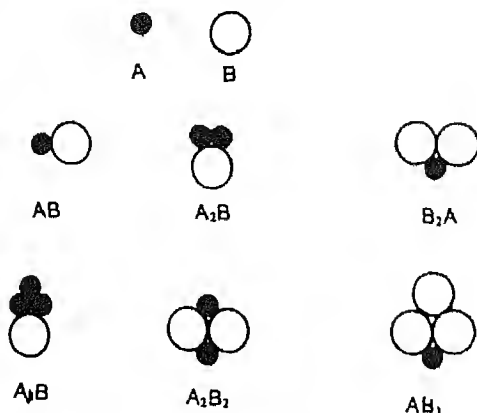Consider the following problem (see Fig 1.3).

Fig 1.3 *Some of the possible combinations of balls A and B*

Set 1 contains several identical small balls A each weighing 1 g.
Set 2 contains several identical medium balls B each weighing 5 g.

Experiment I Suppose the balls have hooks such that A-type balls can be joined to
the B-type to form a combination system AB. What mass relationships will be
observed between A, B, and AB?

    (a) It is clear that if one A and one B are taken separately, the sum of their
masses is 6 g. The combination AB will also weigh 6 g. If we combine
two As with two Bs to obtain two ABs, the mass before the combination
will be 12 g and the mass after the combination will also be 12 g. In
other words, the mass before and after the combination remains the same
as long as no additional balls are either added or taken away during the
combination process. We will call this result the LAW OF CONSERVATION
OF MASS since it expresses the fact that mass neither increases nor
decreases during the combination process.

    (b) If we take one AB (which weighs 6 g) and pull it apart, it is found that B
(which weighs 5 g) contributes $5/6 \times 100$, i.e., 83.33% of the mass, and
A (which weighs 1 g) contributes $1/6 \times 100$, i.e., 16.67% of the mass. The
same ratio is obtained with any AB type of combination system. This
observation may be stated as the LAW OF CONSTANT COMPOSITION which
expresses the fact that the mass ratio of the constituents is the same in a
combination system no matter which sample is analysed.

Experiment II Suppose that in addition to the system AB, it is possible to join two
A balls with one B ball to yield another joint system A_2B. What mass

relationships will be observed between A, B, AB, and A_2B?

It is easy to verify that the law of conservation of mass and the law of constant composition are both true for the following processes:

$$A+B \rightarrow AB$$
$$A+A+B \rightarrow A_2B$$
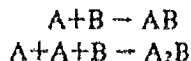
In addition, an interesting regularity is found if we compare the masses of B in AB and A_2B which combine with a fixed mass of A. Taking 1 g of A as the reference, it is found that 5 g of B is needed in AB but only 2.5 g is needed in A_2B. The two masses of B (i.e., 5 g and 2.5 g) are simple multiples of each other (i.e., 2:1). This observation will be called the LAW OF MULTIPLE PROPORTIONS (Carry out similar calculations for different combinations like AB_2, A_3B, etc. shown in Fig. 1.3. Verify that masses of B in all these cases, which combine with a fixed mass of A, are related to each other as simple multiples).

If you analyse the logic of the above examples, it will be obvious that the three laws are straightforward consequences of only two features·

(i) that the balls do not fragment during the association and the dissociation process, and

(ii) all the A type balls are identical and so are the B·type balls

It follows that as long as these features are valid, the three laws will be followed. If we use identical grains of wheat and rice, or identical stones and marbles, the laws will be obeyed; it does not matter what the weights of the identical objects are. In short, the crucial requirements for the laws are *discreteness* and *identity*.

If we are dealing with objects which can be seen and handled, the discreteness and identity are visible. In such cases, establishing the laws by weighing can always be carried out but the logic of the argument is so clear and simple, that we can accept the result even without doing the 'experiment'. At the level of atoms and molecules, nothing is visible. We have, therefore, to rely on indirect evidence. The greatness of Lavoisier's work lies in the fact that he showed that weighing of substance is a powerful way of studying chemical behaviour. The greatness of Dalton's work is that he showed that since the regularities observed in mass relations are like the three laws given above, it suggests discreteness and identity at the invisible level. The idea that atoms exist was thus born.

1.3.2 Experimental Basis for the Laws of Chemical Combination

Let us begin by looking at some experimental facts. Chemical reactions show a baffling variety. Different substances react under different conditions to yield

different products Such a vast study would be a hopeless task unless we found some patterns It turns out that mass relationships between reactants and products show some beautiful regularities which are obeyed by *all* chemical reactions.

'(i) *Law of conservation of mass:* In every chemical reaction, the mass before and after the reaction is the same

(ii) *Law of constant composition.* All pure samples of the same compound contain the same elements combined in the same proportion by mass For example, a pure sample of water, irrespective of the source, always yields on decomposition 88.89% by mass of oxygen and 11.11% by mass of hydrogen

(iii) *Law of multiple proportion:* Copper and oxygen combine to form two oxides, the red cuprous oxide and the black cupric oxide. If pure samples of the two are analysed for their copper and oxygen contents, it is found that in the red oxide, 8 g of copper are present for every gram of oxygen (i e , the mass ratio of copper to oxygen is 8:1), but in the black copper oxide, only 4 g of copper are present for every gram of oxygen (i.e., the mass ratio is 4:1). The amount of copper that combines with 1 g of oxygen in the first case (i.e., 8 g) is a simple multiple of the amount that combines in the second case (i e , 4 g). Such simple ratios are always observed whenever two elements form more than one compound.

Recall now the two simple experiments discussed in section 1.3.1. It was shown there that a combination process involving objects (namely balls) which are discrete, unbreakable, and identical, yield the law of conservation of mass, the law of constant composition, and the law of multiple proportion. The same three laws are found to be obeyed in all chemical processes The inference from this observation should be obvious. It is that matter consists of discrete particles (atoms) which do not break up during a chemical transformation. Further, atoms of the same element are alike. And finally, formation of compounds from elements indicates that two or more atoms join together to give combination systems (molecules).

Gay-Lussac's Law. In addition to mass relationships described above, chemical reactions between gases show interesting volume relationships. This was discovered by the French chemist, Gay-Lussac who found that the volumes of the reactants and products in a large number of chemical reactions are related to each other by small integers, provided the volumes are measured at a common temperature and pressure. For example, in the reaction of hydrogen gas with oxygen gas to produce water vapour, it was found that two volumes of hydrogen and one volume of oxygen will

give two volumes of water vapour. Gay-Lussac's discovery of integer ratios in volume relationships is actually the law of definite proportions by volume. The law of definite proportions stated earlier was with respect to mass

1.3.3   Dalton's Model of an Atom

John Dalton, an English school teacher in Manchester, was the first scientist who suggested in 1804 that the laws of chemical combination point to the existence of atoms. His ideas can be summarised as follows:

  (i) Atoms of a particular element are all alike but differ from atoms of another element. This feature is suggested by the fact that different elements have different behaviour but different samples of the same element have the same behaviour.

  (ii) An atom of an element has a fixed mass. This is suggested by the fact that a fixed quantity of an element (which must contain a fixed number of atoms) has a fixed mass.

  (iii) Atoms are indestructible, i.e., they can neither be created nor be destroyed

The first postulate of Dalton along with the fact that there are about 100 elements, means that there are only about 100 distinct types of atoms. How can we then explain the existence of millions of compounds? We postulate that the smallest unit of a compound is not individual atoms, but a *group of atoms*. The name given to such a group of atoms, capable of independent existence, is *molecule*.

We have formed, at this stage, a picture of the structure of matter in terms of atoms and molecules. Such a picture immediately raises a number of questions. If atoms have mass, how can we determine it? Do atoms have a shape? Are they like spherical balls? What is inside the atoms? What is the size of atoms? Why and how do atoms combine to form molecules? How are the atoms arranged in molecule? The questions can go on and on In trying to solve one mystery, we have created many more. This is one of the characteristics of science. Solution of the one problem very often gives rise to new problems which are more complicated and more puzzling than the original problem. This may look like discouraging situation to some, but to those who love to understand natural phenomena, nothing could be more exciting.

In about the last two hundred years since Dalton, chemists and physicists have been raising questions of the type given above. The knowledge obtained so far shows that the atomic molecular view is correct but some modifications in Dalton's idea of atoms and molecules are necessary. For example, the discovery of isotopes (atoms

of an element with different masses) has shown that the atoms of the same element are not alike. Similarly, the discovery of nuclear reactions has made it possible to transform mass into energy Atoms, therefore, cannot be regarded as indestructible. However, in chemical reactions (as against nuclear reactions) only a negligible amount of mass is transformed into energy. We therefore continue to consider atoms as indestructible as far as chemical reactions are concerned. In subsequent courses of chemistry and physics, we shall be learning more and more about the fascinating story of atoms For the time being, we shall concentrate on the first question, namely, 'If atoms have mass, how can we determine it?'

1.4 ATOMIC MASS

It is clear that since individual atoms cannot be seen and isolated, we cannot directly weigh an atom The mass of an atom therefore must be obtained indirectly If we take a sample of an element large enough to be weighed and also count the number of atoms in it, we can find the mass of a single atom by dividing the total mass by the number of atoms. Unfortunately, there was no direct way available to count the number of atoms, so this method was also not practical The problem seemed hopeless until a solution was suggested by the Italian chemist, Amedeo Avogadro in 1811.

Avogadro's hypothesis: Suppose we have equal volumes of two gases (say hydrogen and nitrogen) in two flasks and weigh them at the same temperature and pressure We will find that the masses are different. The following explanations can be proposed to explain this observation (a) There are different numbers of particles (atoms or molecules) in the two jars but the particles of hydrogen and nitrogen have the same mass. (b) The mass of a particle of hydrogen is different from the mass of a nitrogen particle but the number of particles in the two flasks is the same. (c) The mass of the particles as well as their numbers are different These three possibilities are shown in Fig 1 4 (a,b,c)

hydrogen   (a)   nitrogen
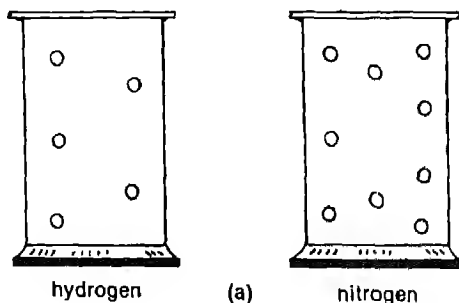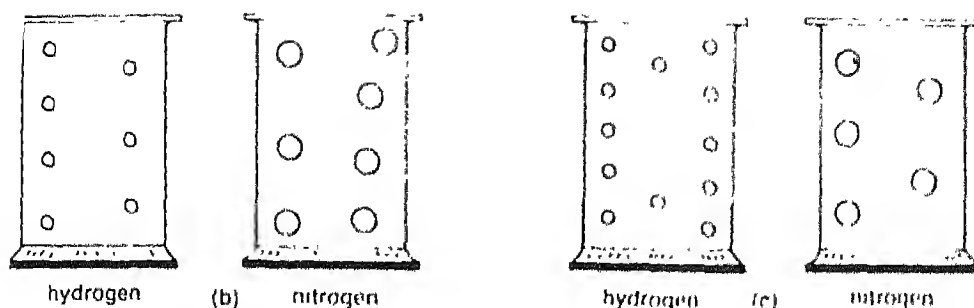
Fig. 1.4   Three possibilities (a, b, c) to explain the difference in mass of equal volumes of hydrogen and nitrogen at the same temperature and pressure. (a) mass is the same but numbers are different, (b) the number of particles is the same but mass is different, (c) both numbers and mass are different

Avogadro made an inspired guess that the second possibility (b) is the correct one. He rejected the first one as it seems unlikely that the particles of different gases should have the same mass. He rejected the third one because it was the most complicated explanation. (A scientist, as everybody else, likes a simple solution).

The statement that equal volumes of all gases at the same temperature and pressure contain equal number of particles is called Avogadro's Hypothesis. This idea was a guess on the part of Avogadro, but later developments have fully confirmed it.

The volume relationship observed in the reactions involving gases can be made to yield new information in the light of Avogadro's hypothesis. For example, it is known that at the same temperature and pressure,

1 volume of oxygen + 2 volumes of hydrogen   2 volumes of water vapour

If equal volumes contain an equal number of particles and if a unit volume has n particles then the above equation can also be written as,

n particles of oxygen + 2n particles of hydrogen = 2n particles of water vapour

or   1 particle of oxygen + 2 particles of hydrogen = 2 particles of water vapour

This means that 1 particle of water contains 1/2 particle of oxygen. If the particle of oxygen is an atom of oxygen, this would mean that an atom can be subdivided. But the main point of atomic theory is that the atom is the smallest particle and hence cannot be broken further, i.e., atoms are indestructible. There is one way out of the difficulty. Suppose the particle of oxygen is not a single atom but contains two atoms under normal conditions. There is no conflict then between Dalton's and Avogadro's ideas, because half particle of oxygen would mean a single

atom and not half atom. We have earlier called groups of atoms as molecules. The above analysis shows that the individual particles of oxygen gas are molecules, each molecule containing two oxygen atoms. (Some of you may object that the above analysis does not prove that oxygen molecule must necessarily contain two atoms but it only proves that the number of atoms must be a multiple of two. This objection is certainly true. In the beginning, the choice of two atoms was made because it was the simplest possibility. Later developments have proved that this choice is correct.)

The volume data of the hydrogen-chlorine reaction showed in a similar fashion that the hydrogen molecule is also diatomic, i.e., it contains two atoms. The hydrogen-oxygen reaction can now be rewritten as

  1 molecule of oxygen $+$ 2 molecules of hydrogen $=$ 2 molecules of water vapour
That is,

$$O_2 + 2H_2 = 2H_2O$$
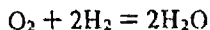
The formula of water molecule must therefore be H_2O.

We have earlier seen from the experimental study of the decomposition of water that 88.89% of its mass is due to oxygen while 11.11% is due to hydrogen, i.e., mass ratio of oxygen and hydrogen is nearly 8:1. The formula H_2O for water shows that in every molecule of water there are 2 atoms of hydrogen and 1 atom of oxygen. It follows therefore that an atom of oxygen is 16 times heavier than an atom of hydrogen. This method cannot give the absolute mass of a hydrogen atom or of an oxygen atom but it does give their relative masses. A more accurate analysis shows that if the hydrogen atom mass is taken as one, then the oxygen atom mass is 15.88. It should be clearly understood that these numbers are only *relative* to each other and therefore they do not tell us what the mass of a hydrogen atom is in grams or ounces or any other unit. For example, suppose we are told that Ram's height is 1.1 times Shyam's height. Now 1.1 is a relative number, i.e., a ratio; it tells us nothing about what the actual height of Ram or Shyam is. However, if we are also told that Shyam is 1.50m tall, then we can at once say that Ram is 1.65m tall.

WHAT ARE ISOTOPES?

Dalton assumed that the atom is indivisible, but the discovery of the electron in the late nineteenth century showed that an atom has an internal structure. We will study details of the atomic structure in Unit 4,

Here we give a short summary to clarify the meaning of the term ISOTOPE.

It is now known that an atom consists of negatively charged electrons and a positively charged nucleus. The total negative charge due to electrons is equal to the positive charge of the nucleus, the atom is therefore, on the whole, a neutral entity. Electrons are very light and do not contribute to the mass of an atom which is essentially the nuclear mass. Although the detailed structure of the nucleus is not yet fully understood, it is adequate to regard it as made of positively charged protons, and a certain number of uncharged neutrons. The charge on a proton is equal and opposite to the charge on an electron whereas the mass of a proton is very nearly equal to the mass of neutron. To summarize

(i) Protons contribute to the positive charge of a nucleus, the number of protons in a nucleus is called the atomic number Z.

(ii) Protons and neutrons contribute to the mass of a nucleus, the total number of protons and neutrons is called the mass number A.

(iii) The number of electrons in an atom is equal to the number of protons in its nucleus.

(iv) The mass of an atom is essentially the mass of its nucleus.

By convention, the atomic number is written at the bottom left corner of the symbol of the atom, and the mass number is written at the top left corner. For example, the symbol $^{12}_{6}C$ means that the atomic number of the nucleus of a carbon atom is 6 and its mass number is 12. It follows that the nucleus of a carbon atom has 6 protons, 12-6 (i.e., 6) neutrons, and 6 electrons. It is now possible to give a more exact definition of the term ELEMENT. *An element is defined as a substance whose atoms have the same atomic number.*

The above definition implies that all the atoms of a given element must have nuclei containing the same number of protons. However it is not necessary that they contain the same number of neutrons. For example, all oxygen atoms have $Z = 8$. This means that all oxygen atoms must have 8 protons and 8 electrons. But it so happens that three varieties of oxygen atoms are found in nature which differ in the number of neutrons in their nuclei. These varieties, designated as ISOTOPES of oxygen, are:

$^{16}_{8}O$ atoms with 8 protons and 8 neutrons

$^{17}_{8}O$ atoms with 8 protons and 9 neutrons

and $^{18}_{8}O$ atoms with 8 protons and 10 neutrons

In short, isotopes of an element are atoms of the elements with the *same* atomic number but *different* mass number.

Following Dalton's pioneering work, the Italian chemist Stanislao Cannizaro made systematic use of Avogadro's hypothesis, Gay-Lussac's law and the vapour density data to determine a large number of relative atomic masses. In this scheme, hydrogen was taken as reference and assigned the arbitrary value of 1. It was observed that if, instead, oxygen was taken as the reference and assigned the value of 16, then the (relative) atomic masses of most of the other elements came very close to whole numbers. Because of this convenience, oxygen was adopted as the standard. The modern atomic mass scale, adopted in 1961, is based on carbon-12 standard.

The accurate determination of atomic masses is now done with an instrument called MASS SPECTROMETER.* This instrument, invented early in this century, determines atomic masses from the deflection of atomic ions in electric and magnetic fields. Using the mass spectrometer, it was observed that most elements consist of atoms of more than one mass, i.e., they consist of ISOTOPES (see Unit 3 for further discussion of isotopes). Isotopes are atoms of the same element having different masses. Naturally occurring carbon has three isotopes called carbon-12, carbon-13 and carbon-14. The modern-atomic-mass scale assigns a mass of exactly 12 atomic mass units to the carbon-12 isotope. ONE ATOMIC MASS UNIT (amu), therefore, is equal to one-twelfth of the mass of one carbon-12 atom. Naturally occurring carbon is a mixture of isotopes. The average mass of a carbon atom in such a sample is 12 011 amu. The average atomic mass for a naturally occurring element, expressed in atomic mass units, is called its ATOMIC MASS. Table 1.4 gives the atomic masses of elements.

1 4.1 Mole Concept

The table of atomic masses referred to above gives relative masses. A question which naturally follows at this stage is, "What is the absolute mass of individual atoms?" To answer this question, we make use of the mole concept which you have studied in earlier classes.

---

*The mass spectrometer is one the most useful tools in modern chemistry for determining masses of molecules and molecular fragments. You will study more about the use of this instrument in chemistry in advanced courses

TABLE 1 4

Atomic Masses of Elements referred to $^{12}C = 12.0000$

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)	Mercury	Hg	80	200 6
Aluminium	Al	13	27 0	Molybdenum	Mo	42	95.9
Americium	Am	95	(243)	Neodymium	Nd	60	144 2
Antimony	Sb	51	121 8	Neon	Ne	10	20.2
Argon	Ar	18	39 9	Neptunium	Np	93	237 0
Arsenic	As	33	74 9*	Nickel	Ni	28	58.7
Astatine	At	85	(210)	Niobium	Nb	41	92.9
Barium	Ba	56	137 3	Nitrogen	N	7	14 0
Berkelium	Bk	97	(245)	Nobelium	No	102	(254)
Beryllium	Be	4	9 01	Osmium	Os	76	190 2
Bismuth	Bi	83	209 0	Oxygen	O	8	16.0
Boron	B	5	10 8	Palladium	Pd	46	106.4
Bromine	Br	35	79 9	Phosphorus	P	15	31.0
Cadmium	Cd	48	112 4	Platinum	Pt	78	195,1
Caesium	Cs	55	132 9	Plutonium	Pu	94	(242)
Calcium	Ca	20	40 1	Polonium	Po	84	(210)
Californium	Cf	98	(251)	Potassium	K	19	39 1
Carbon	C	6	12.0	Praseodymium	Pr	59	140 9
Cerium	Ce	58	140 1	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.5	Protactinium	Pa	91	231.0
Chromium	Cr	24	52 0	Radium	Ra	88	226.0
Cobalt	Co	27	58 9	Radon	Rn	86	(222)
Copper	Cu	29	63 5	Rhenium	Re	75	186.2
Curium	Cm	96	(245)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162 5	Rubidium	Rb	37	85.5
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101 1
Erbium	Er	68	167 3	Samarium	Sm	62	150.4
Europium	Eu	63	152 0	Scandium	Sc	21	45 0
Fermium	Fm	100	(254)	Selenium	Se	34	79.0
Fluorine	F	9	19.0	Silicon	Si	14	28.1
Francium	Fr	87	(223)	Silver	Ag	47	107.9
Gadolinium	Gd	64	157.3	Sodium	Na	11	23.0
Gallium	Ga	31	69.7	Strontium	Sr	38	87.6
Germanium	Ge	32	72.6	Sulphur	S	16	32.1
Gold	Au	79	197.0	Tantalum	Ta	73	180.9
Hafnium	Hf	72	178 5	Technetium	Tc	43	98.9
Helium	He	2	4.00	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.008	Thallium	Tl	81	204 4
Indium	In	49	114 8	Thorium	Th	90	232 0

TABLE 1 4 *(Contd)*

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Iodine	I	53	126 9	Thulium	Tm	69	168 9
Iridium	Ir	77	192 2	Tin	Sn	50	118 7
Iron	Fe	26	55 8	Titanium	Ti	22	47 9
Krypton	Kr	38	83 8	Tungsten	W	74	183.8
Lanthanum	La	57	138 9	Uranium	U	92	238 0
Lawrencium	Lr	103	(257)	Vanadium	V	23	50 9
Lead	Pb	82	207 2	Xenon	Xe	54	131 3
Lithium	Li	3	6 94	Ytterbium	Yb	70	173 0
Lutetium	Lu	71	175 0	Yttrium	Y	39	88 9
Magnesium	Mg	12	24 3	Zinc	Zn	30	65 4
Manganese	Mn	25	54 9	Zirconium	Zr	40	91 2
Mendelevium	Md	101	(256)				

Numbers in parentheses give the mass number of the most stable isotope

It will be useful to recollect the logic of the mole concept The mass of an oxygen molecule (O_2) relative to the mass of a hydrogen molecule (H_2) is 32.00 : 2 02. If one sample of O_2 weighs 32 grams and another sample of H_2 weighs 2.02 grams, we know that the two samples contain the same number of molecules. If the first sample contains N molecules, so does the second sample. This constant N is called the Avogadro's constant. Its value has been determined experimentally and found to be 6.02×10^{23} Because of the great significance of 6.02×10^{23} atoms or molecules, the amount of any substance containing this number of atoms or molecules is given a special name—A MOLE (abbreviated mol) of the substance. The SI definition of mole is as follows:

The mole is the amount of any substance that contains as many elementary entities as there are atoms in exactly 0 012 kg (i.e., 12 g) of carbon-12. When the mole is used, the elementary entities must be stated. They may be atoms, molecules, ions, electrons, or any other entity.

A useful quantity in chemistry is the MOLAR MASS which is the mass of one mole From the definition of a mole given above, we reach the important conclusion that *the molar mass in grams of any atom is numerically equal to its relative atomic mass in amu.* In other words, from the table of atomic masses, we can immediately get the molar mass in grams which in turn is the mass of 6.02×10^{23} atoms. From this information, it is easy to calculate the absolute mass of one atom as shown below. From the table of atomic masses, we can also calculate the relative molecular mass in amu of a molecule if the formula of the molecule is known The molar mass in grams of any molecule is numerically equal to its relative molecular mass in amu.

In this case since the molar mass in grams is the mass of 6.02×10^{23} molecules, the absolute mass of one molecule can be easily calculated (see Example 1.3).

Example 1.1

Calculate the mass of a carbon atom and of a silver atom

Solution

Mass of a carbon atom   12.01 amu
Mass of one mole of carbon atoms   12.01 g
This means that mass of 6.02×10^{23} ^{12}C atoms = 12.000 g

The mass of a single ^{12}C atom $= \dfrac{12.000}{6.02 \times 10^{23}}$

$$= 1.99 \times 10^{-23} \text{ g}$$

In the same manner, since the atomic mass of silver is 107.87 amu, the mass of a

silver atom $= \dfrac{107.87}{6.02 \times 10^{23}} = 17.92 \times 10^{-23} \text{g}$

(Note For silver, the mass represents the weighted average of isotopic masses)

Example 1.2

Determine the number of atoms in 1.792×10^{-6} g of silver.

Solution

Mass of silver atom (see Example 1.1) $= 17.92 \times 10^{-23}$ g
Number of atoms of silver in 1.792×10^{-6} g of silver

$$= \dfrac{1.792 \times 10^{-6}}{17.92 \times 10^{-23}} = 10^{16}$$

Example 1.3

Compute the mass of one molecule and the molecular mass of C_6H_6 (benzene).

Solution

Molecular mass $= 6 \times$ atomic mass of C $+ 6 \times$ atomic mass of H
$= 6 \times 12.01 + 6 \times 1.008$
$= 72.06 + 6.048$
$= 78.11$ amu

Mass of one molecule of $C_6H_6 = 6 \times$ mass of C atom $+ 6 \times$ mass of H atom
$= 6 \times 1.99 \times 10^{-23} + 6 \times 1.67 \times 10^{-24}$
$= 11.94 \times 10^{-23} + 10.02 \times 10^{-24}$
$= 12.94 \times 10^{-23}$ g

The mass of one molecule of C_6H_6 can also be obtained by dividing the molar mass of C_6H_6 by Avogadro's constant.

The fact that a mole is related to the number of particles means that it must also be related to the volume of gases because equal volumes of all gases at the same temperature and pressure contain an equal number of particles. This is indeed supported by experiments. It is found that at $0°C$, and 1 atmosphere pressure, known as standard temperature and pressure (STP), one mole of all gases occupies 22.4 litres of volume. The molar volume at STP is thus 22.4 litres.

1.4.2 Determination of Chemical Formulas

All of you know that the formula for water is H_2O, that of hydrochloric acid is HCl and so on. How were these formulas determined? We will now answer this question in a systematic fashion. There are several types of chemical formulas. The first is the empirical formula. It gives the *relative* number of different types of atoms present in a compound. The second type is known as the molecular formula. It expresses the exact number of different atoms in a compound. For example, CH is the empirical formula of benzene and C_6H_6 is its molecular formula.

The empirical formula of a compound can be calculated from (i) chemical analysis of the compound, and (ii) atomic masses of the constituent elements. The result of chemical analysis* is usually expressed as percentage composition (by mass) of the elements in the compound. (Oxygen percentage is usually not given explicitly; it is obtained by subtracting the sum of the percentages of all the other elements from 100.) To calculate the empirical formula, the first step is to convert the given percentage composition to mole composition. This is done by dividing the mass of each element by its atomic mass. From the mole composition we can determine the mole ratio between different elements in the compound. Any fraction in mole ratio is then removed by dividing or multiplying by a suitable number.

Example 1.4

An organometallic compound on analysis was found to contain, C = 64.4%, H = 5.5% and Fe = 29.9%. Determine its empirical formula.

Solution

The sum of percentage is 99.8 (i.e., nearly 100). Therefore, no oxygen is present
Percentage composition by mass is 64.4% C: 5.5% H· 29.9% Fe

---

* There are two types of experiments which provide the required data. Either the compound is synthesised from its elements, or it is broken down into the elements, or into compounds of known composition. The second method is more common. For example, composition of many of the carbon compounds containing only carbon and hydrogen is usually determined by burning them in excess oxygen gas so that all of the carbon in the original compound is converted to carbon dioxide and the hydrogen is converted to water. By weighing the amount of carbon dioxide and water formed, the amount of carbon and hydrogen in the original compound can be determined.

$$\text{Mole Ratio} = \frac{64.4}{12.01} \text{ C}: \frac{5.5}{1.008} \text{ H}: \frac{29.9}{55.85} \text{ Fe}$$

$$= 5.36 \text{ C}: 5.45 \text{ H}: 0.535 \text{ Fe}$$

Dividing by 0.535, we get mole ratio = 10.02 C: 10.19 H: 1 Fe

$$= 10 \text{ C}: 10 \text{ H}: 1 \text{ Fe}$$

Therefore, empirical formula is $C_{10}H_{10}$ Fe.

Example 1.5

Four grams of copper chloride on analysis was found to contain 1.890 g of copper (Cu) and 2.110 g of chlorine (Cl). What is the empirical formula of copper chloride?

Solution

Percentage of copper in copper chloride $= \frac{1.890}{4} \times 100 = 47.3\%$

Percentage of chlorine in copper chloride $= \frac{2.110}{4} \times 100 = 52.7\%$

Percentage composition is 47.3% Cu and 52.7% Cl.

Mole ratio $= \frac{47.3}{63.55} \text{ Cu}: \frac{52.7}{35.45} \text{ Cl} = 0.743 \text{ Cu}: 1.487 \text{ Cl}$

Dividing by 0.743, mole ratio $= 1 \text{ Cu}: 1.999 \text{ Cl}$

$$= 1 \text{ Cu}: 2 \text{ Cl}$$

Therefore, the empirical formula is $CuCl_2$.

The molecular formula of a compound can be calculated from (i) the molecular mass of the compound, and (ii) the empirical formula of the compound.

Example 1.6

The molecular mass of benzene is 78 and its percentage composition is 92.3% C and 7.69% H. Determine the molecular formula of benzene.

Solution

Percentage composition = 92.3% C: 7.69% H

Mole ratio $= \frac{92.3}{22.01} \text{ C}: \frac{7.69}{1.008} \text{ H}$

$$= 7.69 \text{ C}: 7.63 \text{ H}$$

Dividing by 7.63 gives 1.008 C: 1 H (= 1 C: 1 H). Therefore, the empirical formula is CH or the molecular formula is $(CH)_n$.

Empirical formula mass = 12.01 + 1.008

$$= 13.018 \text{ amu}$$

n = mol mass/13.018 = 78/13.018 = 5.99 ≈ 6

Therefore, the molecular formula is C_6H_6.

Knowing the molecular formula, one can determine the number of moles (or

number of molecules) in a given amount of that compound

Example 1 7

Calculate the number of moles and the number of molecules in 8 516 g of ammonia (NH_3).

Solution

Molecular mass of NH_3 = 14.007 + 3 × 1.008

$$= 17.031 \text{ amu}$$
$$= 17 031 \text{ g/mol ammonia}$$

Therefore, 8 516 g of ammonia = 8.516/17.031 mol ammonia

$$= 0.5000 \text{ mol ammonia}$$

One mol of a substance has 6 02 × 10^{23} molecules

Therefore, 0.5000 mol has 3 01 × 10^{23} molecules

Example 1 8

Calculate the number of grams of oxygen in 0 10 mol of Na_2CO_3 $10H_2O$

Solution

One mol of $Na_2CO_3.10H_2O$ has 13 mol of oxygen atoms. Therefore, in 0 10 mol of $Na_2CO_3.10H_2O$, there will be 1.3 mol of oxygen atoms.

One mol of oxygen atoms = 16 g

Therefore, 1 3 mol of oxygen atoms = 16 × 1.3 = 20 8 g

1 5 CHEMICAL EQUATION

When the substances taking part in a chemical reaction are represented by their molecular formulas, the chemical reaction can be written in the form of a chemical equation Equations express the qualitative and quantitative information about chemical reactions in a simple manner. The quantitative aspects, dealing with the mass and volume relations among reactants and products, is termed stoichiometry*. We shall now show how a chemical equation is written and what information it conveys so that we can discuss stoichiometric calculations.

1 5.1 Writing a Balanced Chemical Equation

The chemical reaction between hydrogen and oxygen to produce water can be written as Hydrogen + Oxygen = Water. However, this way of expressing a chemical reaction can be simplified by using chemical formulas. Thus, the above reaction can be written as $H_2 + O_2 = H_2O$. However, this equation does not obey the law of conservation of mass because there are two atoms of oxygen on the left-hand side while there is only one atom of oxygen on the right-hand side. For a chemical equation to be correct, the number of atoms of each element must be the same on both sides of the equation An equation satisfying this requirement is called

---

* Stoichiometry is derived from Greek words meaning 'to measure an element'

a balanced chemical equation*. By choosing suitable coefficients, a balanced equation for the above reaction can be written in any of the following forms:

$$H_2 + \frac{1}{2}O_2 \quad H_2O \qquad \qquad . \quad (i)$$

$$2H_2 + O_2 \quad 2H_2O \qquad \qquad . \quad (ii)$$

$$4H_2 + 2O_2 \quad 4H_2O \qquad \qquad ... \quad (iii)$$
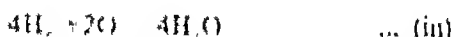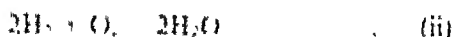
However, by convention, equations are written in a form in which the coefficients are the *smallest* whole numbers. The reaction between hydrogen and oxygen to give water is thus represented by equation (ii)

As another example of balancing an equation, we consider the reaction,

$$C_2H_6O + O_2 \qquad CO_2 \qquad + H_2O$$

Ethyl alcohol + oxygen   Carbon dioxide + Water
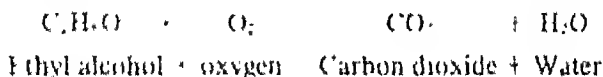
To balance carbon atoms, we write

$$C_2H_6O + O_2 \quad 2CO_2 + H_2O$$

and to balance hydrogen atoms, we write

$$C_2H_6O + O_2 \quad 2CO_2 + 3H_2O$$

Oxygen atoms can be balanced by multiplying O_2 by 3. Thus, we have the balanced equation.

$$C_2H_6O + 3O_2 \quad 2CO_2 + 3H_2O$$

It is frequently convenient to know the physical state (i.e., solid, liquid or gas) of each reactant and product. This information will be a necessity, when we later discuss the energy changes during chemical reactions. The following abbreviations are used to indicate the physical state of the reactants and products:

(s) = solid, (l) = liquid, (g) = gas or vapour, (aq) = aqueous solution.

Thus, the reactions given earlier can be written more precisely as,

$$2H_2(g) + O_2(g) \quad 2H_2O\ (g)$$

and $$C_2H_6O\ (l) + 3O_2(g) \quad 2CO_2\ (g) + 3H_2O\ (l)$$
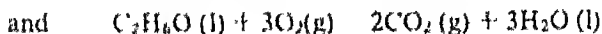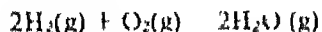
Additional information about heat absorbed or evolved, temperature, pressure etc.,

---

*When equations contain charged species (e.g., ions), they must satisfy the charge conservation also. This aspect will be considered later.

can also be incorporated in a chemical equation. This will be considered later at appropriate places.

1.5 2   Significance of Chemical Equations

A balanced equation contains much quantitative information because it can be interpreted in a number of ways. Let us first consider reactions in which all the participants are gases. For instance, the equation,

$$2H_2(g) \quad + \quad O_2(g) \quad = 2H_2O, \text{ means·}$$
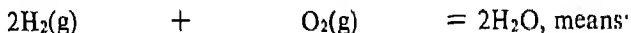
2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam,

or $2(6.02 \times 10^{23})$ molecules of hydrogen + $1(6\ 02 \times 10^{21})$ molecules of oxygen
$$= 2(6.02 \times 10^{23}) \text{ molecules of steam}$$

or 2 mol of hydrogen + 1 mol of oxygen = 2 mol of steam
or 4.032 g of hydrogen + 32.00 g of oxygen = 36.03 g of steam
or 44 8 litres of hydrogen + 22 4 litres of oxygen
$$= 44\ 8 \text{ litres of steam (at STP)}$$

Thus, a chemical equation for a gaseous reaction gives quantitative details about reactants and products in terms of (i) molecules (or atoms), (ii) moles, (iii) grams, and (iv) volumes (if any of the participants are in the gaseous form)

1 5 3   Calculations Using Chemical Equation

A balanced chemical equation permits calculation of the masses of the reactants and the products. Let us consider the equation representing the reaction between hydrogen and oxygen.to yield water. The balanced equation for this reaction is

$$2H_2 + O_2 \rightarrow 2H_2O$$
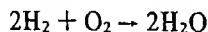
This equation can be interpreted in any of the following ways

2 molecules H_2+1 molecule O_2 → 2 molecules H_2O
4 032 amu H_2+32 00 amu O_2 → 36 03 amu H_2O
2 mol H_2+1 mol O_2 → 2 mol H_2O
2 $(6\ 02 \times 10^{23})$ molecules H_2+1 (6.02×10^{23}) molecules O_2 $2(6.02 \times 10^{23})$ molecules

of H_2O

4 032 g H_2+32 00 g O_2 → 36 03 g H_2O

Each of these forms can be expressed in words. For example, the last form means that 4.032 g of hydrogen react with 32 00 g of oxygen to yield 36.03 g of water.

We can, of course, choose any unit for mass. Thus in terms of pounds (lbs), the above equation will mean

$$4.032 \text{ lbs } H_2 + 32.00 \text{ lbs } O_2 \rightarrow 36.03 \text{ lbs } H_2O$$

Quantitative information of different kinds about the amount of reactants and products can be easily obtained from a chemical equation as shown by the following examples.

Example 1 9

How many grams of chlorine (Cl_2) are required to completely react with 0.400 g of hydrogen (H_2) to yield hydrogen chloride (HCl)? Also calculate the amount of HCl formed.

Solution

The balanced equation for the reaction is

$$H_2 + Cl_2 \rightarrow 2HCl$$

Now, 0 400 g of $H_2 = \dfrac{0.400}{2.016}$ mol of H_2

$$= 0.198 \text{ mol of } H_2$$

It follows from the equation that
0.198 mol H_2 + 0.198 mol $Cl_2 \rightarrow$ 0.396 mol HCl
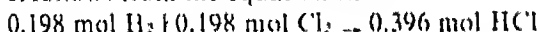
Since 1 mol $Cl_2 = 70.90$ g Cl_2 and 1 mol HCl $= 36.46$ g HCl
     0 198 mol $Cl_2 = 0.198 \times 70.90$ g Cl_2
                    $= 14.00$ g Cl_2
and 0.396 mol HCl $= 0.396 \times 36.46$ g HCl
                    $= 14.4$ g HCl

Notice that the law of conservation of mass is obeyed as 0 400 g of H_2 combines with 14.0 g of Cl_2 to yield 14 4 g of HCl. Indeed, we could have calculated the amount of HCl by adding the masses of H_2 and of Cl_2 instead of first calculating the moles of HCl.

Very often the reacting substances are not present in exactly the same proportions as required by the balanced equation. Consider the reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$
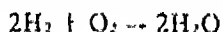
If the reaction mixture consists of 2 mol of H_2 and 2 mol of O_2, it is obvious that only 1 mol of O_2 will be used up and 1 mol of O_2 will be left over. In such a case, hydrogen is said to be the LIMITING REACTANT because its concentration limits the amount of the product. The following problem is an example of a reaction with a limiting reactant where the masses of the reactants are given rather than the number of moles

Example 1.10

3.00 g of H_2 react with 29.00 g of O_2 to yield H_2O.
   (i) Which is the limiting reactant?
   (ii) Calculate the maximum amount of H_2O that can be formed.
   (iii) Calculate the amount of one of the reactants which remains unreacted.

Solution

We first express each of the masses in moles. Since molar mass of $H_2 = 2.016$ g and molar mass of $O_2 = 32.00$ g, it follows that

$$3.00 \text{ g of } H_2 = \frac{3.00}{2.016} \text{ mol of } H_2$$

$$= 1.49 \text{ mol of } H_2$$

and 29.00 g of $O_2 = \frac{29.00}{32.00}$ mol of O_2

$$= 0.9062 \text{ mol of } O_2$$

The balanced equation for the reaction is

$$2H_2 + O_2 = 2H_2O$$
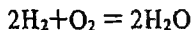
1.49 mol of H_2 require $\frac{1.49}{2}$ (= 0.745) mol of O_2 to yield 1.49 mol of H_2O. Since more oxygen is present than required, it follows that
   (i) Hydrogen is the limiting reactant
   (ii) The maximum amount of water that can be found is 1.49 mol of H_2O.
   (iii) (0.906-0.745) mol, i.e., 0.161 mol of O_2 will be left over in unreacted form in the reaction mixture.

Since reactions in solutions are by far the most common, we turn now to chemical calculations involving solutions. The first question to consider is how to express the amount of a substance present in a given volume of the solution. There are a number of ways of doing this. For example, we can state the concentration of a solution in terms of grams of solute in 100 g of solution. However, the most convenient procedure is to state the number of moles of solute in a given volume of the solution. Thus the MOLARITY of a solute in solution in defined as the number of moles of solute contained in one litre (1L) of solution:

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{Litres of solution}}$$

The units of molarity are moles per litre (mol L^{-1}) or moles per cubic decimetre (mol dm^{-3}) The symbol M is used to designate this MOLAR CONCENTRATION.

Example 1.11

A solution is prepared by dissolving 18.25 g of sodium hydroxide (NaOH) in distilled water to give 1.000 l of solution. Calculate the molarity of NaOH in the solution.

Solution

Molar mass NaOH   40.00 g

18.25 g NaOH $\dfrac{18.25}{40.00}$ mol NaOH

0.4562 mol NaOH

Since this amount of NaOH is present in 1.000 l of solution,

Molarity of NaOH   0.4562 mol L. $^{-}$ 0.4562 M

Example 1.12

A solution is prepared by dissolving 18.25 g of NaOH in distilled water to give 200 cm^3 of solution. Calculate the molarity of NaOH in the solution.

Solution

We have seen in Example 1.11, that 18.25 g of NaOH corresponds to 0.4562 mol NaOH. However, this amount is now present in 200 cm^3 of solution. The amount present in 1.000 L is therefore

$$\frac{0.4562 \times 1000}{200} \text{ mol } \cdot \text{ } 2.281 \text{ mol NaOH}$$

Molarity of NaOH = 2.281 molL. ^{1} 2.281 M

If we take a given volume of a solution of known molarity, we can calculate the amount of solute in this volume of the solution as shown in the next example.

Example 1.13

How many moles and how many grams of sodium chloride (NaCl) are present in 250 cm^3 of a 0.500 M NaCl solution?

Solution

A 0.500 M NaCl contains 00.500 moles of NaCl in 1 L or 1000 cm^3, of solution.

Number of moles of NaCl in 250 $cm^3 = \dfrac{0.500}{4}$ mol NaCl

$= 0.125$ mol NaCl

Molar mass of NaCl = 58.44 g
Mass of 0.125 mol NaCl = 58.44 $\times$ 0.125 g NaCl

$$= 7.30 \text{ g NaCl}$$

The amount of NaCl in 250 cm^3 of 0.500 M NaCl solution

$$= 7\ 30 \text{ g NaCl}$$

It is frequently necessary to know what mass of a solute is needed to make a certain volume of a solution of a given molarity as shown in the next example.

Example 1.14

How many grams of barium chloride (BaCl$_2$) are needed to prepare 100 cm^3 of 0 250 M BaCl$_2$ solution?

Solution,

Molar mass of BaCl$_2$ = 208.2 g

Therefore, 1 L'(or 1000 cm^3) of 1 M BaCl$_2$ solution requires 208.2 g of BaCl$_2$

or   100 cm^3 of 1 M BaCl$_2$ solution requires

$$\frac{208.2 \text{g}}{10} = 20.82 \text{ g BaCl}_2$$

or 100 cm^3 of 0.250 M BaCl$_2$ solution requires $\frac{20.82 \text{g}}{4}$ BaCl$_2$

$$= 5.205 \text{ g BaCl}_2$$

Thus, if 5 205 g of BaCl$_2$ are dissolved in distilled water and the volume is made up to 100 cm^3, the resulting solution will be 0.250 M in barium chloride.

Acids like hydrochloric acid, sulphuric acid, nitric acid are available as concentrated aqueous solutions. The solutions required in the laboratory are prepared by diluting a definite amount of the concentrated acid by a definite amount of water. If the density of the acid is known, it is easy to calculate the molarity of the diluted acid solution.

Example 1.15

Concentrated aqueous sulphuric acid is 98% H$_2$SO$_4$ by mass and has   a density of 1.84 g cm^{-3}. What volume of the concentrated acid is required to make 5.0 l of 0 500 M H$_2$SO$_4$ solution?

Solution

1.0 L of 0 500 M H$_2$SO$_4$ contains 0.500 moles of H$_2$SO$_4$, 5.0 L of 0.500 M H$_2$SO$_4$ contains 2.500 moles H$_2$SO$_4$. Since molar mass of H$_2$SO$_4$ = 98.08 g H$_2$SO$_4$, mass of 2 500 mol H$_2$SO$_4$ = 98.08 $\times$ 2 5 g H$_2$SO$_4$ = 245 g H$_2$SO$_4$

However, concentrated sulphuric acid is 98% by mass. Therefore the amount of concentrated acid which contains 245 g H$_2$SO$_4$ = $\dfrac{245 \times 100 \text{g}}{98}$

$$= 250 \text{ g concentrated acid}$$

The density of the concentrated acid is 1.84 g cm^{-3}. Therefore, the volume in cm^3 containing 250 g of the concentrated acid

$$= \frac{250}{1.84} \text{ cm}^3$$

$$= 136 \text{ cm}^3$$

Thus to get 5.0 L of 0.500 M H_2SO_4 solution, we should take 136 cm^3 of the concentrated acid and make the volume 5.0 litres.

When aqueous solutions are mixed, chemical reactions may take place. The amount of one or more products can be determined if the volumes of the solutions of the reactants and their molarities are known.

Example 1.16

500 cm^3 of 0.250 M Na_2SO_4 solution is added to an aqueous solution of 15.00 g of $BaCl_2$ resulting in the formation of a white precipitate of insoluble $BaSO_4$. How many moles and how many grams of $BaSO_4$ are formed?

Solution

The balanced equation for the reaction is

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2\,NaCl$$

We next find the number of moles of the reactants.
Since 1 L (or 1000 cm^3) of 0.250 M Na_2SO_4 contains 0.250 mol Na_2SO_4,

number of moles in 500 cm^3 of 0.250 M Na_2SO_4 $= \dfrac{0.250}{2}$ mol Na_2SO_4

Mass of 1 mol $BaCl_2$ = 208.2 g
Therefore, number of moles of $BaCl_2$ in 15.00 g $BaCl_2$

$$= \frac{15.00}{208.2} \text{ mol } BaCl_2$$

$$= 0.0720 \text{ mol } BaCl_2$$

The reaction equation shows that 0.0720 mol $BaCl_2$ should react with 0.0720 mol Na_2SO_4 to yield 0.0720 mol $BaSO_4$. (The reaction mixture contains excess of Na_2SO_4; $BaCl_2$ is thus the limiting reactant).
To calculate the mass of $BaSO_4$ in grams, we note that

$$\text{Mass of 1 mol } BaSO_4 = 233.4 \text{ g } BaSO_4$$

$$\therefore \text{ Mass of 0.0720 mol } BaSO_4 = 233.4 \times 0.0720 \text{ g } BaSO_4$$

$$= 16.80 \text{ g } BaSO_4$$

EXERCISES

1 1   State the number of significant figures in each of the following numbers
      (i) $2 653 \times 10^4$ (ii) 0 00368   (iii) 653   (iv) 0 368
      (v) 0 0300

1 2   Express the following numbers to four significant figures.
      (i) 5.607892   (ii) 32 392800   (iii) 1.78986×10^3
      (iv) 0 007837

1.3   Express the result of the following calculations to the appropriate number of significant figures.

      (i) $\dfrac{3\ 24 \times 0\ 08666}{5\ 006}$

      (ii) 0.58 + 324.65
      (iii) $943 \times 0\ 00345 + 101$

1.4   Express the population of India in scientific notation. (Use the 1981 census figure)

1.5   Express each of the following in SI units.
      (i)   93 million miles (This is the distance between earth and sun)
      (ii) 5 feet 2 inches (the average height of an Indian female)
      (iii) 100 miles per hour (the typical speed of Rajdhani Express).
      (iv) 14 pounds per square inch (atmospheric pressure).
      (v)   0 74 $\overset{\circ}{A}$ (the bond length of hydrogen molecule).
      (vi) 46 $\overset{\circ}{}$ C the peak summer temperature in Delhi).
      (vii) 150 pounds (the average weight of an Indian male).

1.6   (a) Classify the following as pure substances or mixtures.
      (b) Separate the pure substances into elements and compounds and divide the
          mixtures into homogeneous and heterogeneous.
          (i) air (ii) milk (iii) graphite (iv) diamond (v) gasoline (vi) tap water (vii) distilled
          water (viii) oxygen (ix) one rupee coin   (x) 22 carat gold   (xi) steel (xii) iron
          (xiii)   sodium chloride (xiv) iodised table salt

1 7   Which of the following mixtures are homogeneous?
      (i) wood (ii) tap water (iii) smoke (iv) soil (v) cloud

1.8   How will you separate the following mixtures?
      (suggest as many methods as you can)
      (i) salt and water (ii) sand and water (iii) oil and water (iv) iron filings and sawdust (v) glass
      powder and sugar.

1.9   (a) When 4.2 g of $NaHCO_3$ (sodium hydrogen carbonate) is added to a solution of
          CH_3COOH (acetic acid) weighing 10 0 g it is observed that 2.2 g of CO_2 is
          released into the atmosphere. The residue left is found to weigh 12.0 g. Show
          that these observations are in agreement with the law of conservation of mass

(b) If 6.3 g of $NaHCO_3$ are added to 15.0 g of CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in the reaction?

1.10 Carbon and oxygen are known to form two compounds. The carbon content in one of these is 42.9% while in the other it is 27.3% Show that this data is in agreement with the law of multiple proportions.

1.11 Calculate the number of atoms in each of the following.
   (i) 52 moles of He
   (ii) 52 amu of He
   (iii) 52 g of He

1.12 KBr (potassium bromide) contains 32.9% by weight potassium. If 6.40 g of bromine reacts with 3.60 g of potassium, calculate the number of moles of potassium which combine with bromine to form KBr.

1.13 Write the empirical formulas of the compounds having the following molecular formulas.
   (i) C_6H_6 (ii) C_5H_{12} (iii) H_2O_2 (iv) H_2O (v) Na_2CO_3 (vi) B_2H_6 (vii) N_2O_4

1.14 Chlorophyll, the green colouring matter of plants responsible for photosynthesis, contains 2.68% of magnesium by weight. Calculate the number of magnesium atoms in 2.00 g of chlorophyll

1.15 (a) Butyric acid contains only C,H, and O. A 4.24 mg sample of butyric acid is completely burned. It gives 8.45 mg of carbon dioxide and 3.46 mg of water. What is the mass percentage of each element in butyric acid?
   (b) If the elemental composition of butyric acid is found to be 54.2% C, 9.2% H, and 36.6% O, determine the empirical formula.
   (c) The molecular mass of butyric acid was determined by experiment to be 88 amu. What is the molecular formula?

1.16 Balance the following equations.
   (i) $H_3PO_4 \rightarrow H_4PO_4 + PH_3$
   (ii) $Ca + H_2O \rightarrow Ca(OH)_2 + H_2$
   (iii) $Fe_2(SO_4)_3 + NH_3 + H_2O \rightarrow Fe(OH)_3 + (NH_4)_2 SO_4$

1.17 (a) A sample of NaOH weighing 0.38 g is dissolved in water and the solution is made to 50.0 cm³ in a volumetric flask. What is the molarity of the resulting solution?
   (b) How many moles of NaOH are contained in 27 cm³ of 0.15 M NaOH?

1.18 Commercially available concentrated hydrochloric acid contains 38% HCl by mass.
   (a) What is the molarity of this solution? The density is 1.19 g cm⁻¹
   (b) What volume of concentrated HCl is required to make 1.00L of 0.10 M HCl?

1.19 The cost of table salt (NaCl) and table sugar ($C_{12}H_{22}O_{11}$) is Rs 2 per kg and Rs 6 per kg respectively. Calculate their costs per mole.

UNIT 2

ELEMENTS, THEIR OCCURRENCE AND EXTRACTION

Mother Earth has everything

OBJECTIVES

In this Unit we shall learn

* the distribution of chemical elements and their occurrence in the earth;

* the importance of chemistry in explaining the occurrence, distribution and composition of chemical elements in the earth;

* the different methods, based on chemical properties to free the elements from their combined states;

* the various processes employed in the extraction of elements;

* qualitative analysis of metals.

ALL MATERIALS found in the earth are composed of chemical elements. Around two-thirds of the elements are metals. Some of the familiar metals used in our daily life are iron, copper, aluminium, tin, lead, gold, silver, nickel and mercury. A few of the non-metals are hydrogen, carbon, oxygen, nitrogen, sulphur and phosphorus. The chemical elements are distributed over the whole of the earth. Some of the elements like nitrogen, oxygen, noble gases and gold occur in the free state or the NATIVE STATE, whilst most other elements occur in the combined state. The reason for this lies in the different chemical reactivities of the elements.

Elements found in the combined state are often present as oxides, carbonates, sulphides and silicates. Table 2.1 lists a few elements and their nature of occurrence.

TABLE 2.1

Elements and Their Occurrence

Elements	Nature of Occurrence
	Oxides
Iron	Iron Oxide (Fe_2O_3) (Haematite)
	Iron oxide (Fe_2O_3, FeO) (Magnetite)
Aluminium	Aluminium oxide hydrate (Al_2O_3, $2H_2O$) (Bauxite)
Manganese	Manganese dioxide (MnO_2) (Pyrolusite)
	Carbonates
Calcium	Calcite ($CaCO_3$)
Magnesium	Dolomite ($MgCO_3$, $CaCO_3$)
Copper	Malachite ($CuCO_3$.$Cu(OH)_2$)
	Silicates
Magnesium	Calcium magnesium silicate ($CaSiO_3$, $3MgSiO_3$) (Asbestos)
	Sulphides
Iron	Iron Sulphide (FeS) (Pyrites)
Copper	Iron copper sulphides (CuS FeS) (Copper pyrites)
Mercury	Mercury sulphide (HgS) (Cinnabar)
Zinc	Zinc sulphide (ZnS) (Zinc blende)
Lead	Lead sulphide (PbS) (Lead glance)

It is interesting to know why certain elements occur as oxides, some as sulphides and others as complex silicates. The reason lies in the chemistry of elements

2.1   EARTH AS A SOURCE OF ELEMENTS

The distribution of elements is different in various parts of the earth (Fig. 2.1). About 80% of the surface of the earth is covered with water and this forms a major source of elements. The sea contains a large number of elements.

The gaseous mixture covering the earth is called the atmosphere. The atmosphere contains mainly nitrogen (78 09%), oxygen (20.95%) and other gases (<1%). The present distribution of elements in the sea and in the atmosphere has been the result of complex chemical reactions that have occurred during the formation of the earth.

The solid phase of the earth, LITHOSPHERE, consists of different types of rocks. The lithosphere forms a major source of elements It is important to understand the occurrence of material in the earth in three different phases (gas, liquid and solid) and the different elemental compositions in the three phases.

The present knowledge of the earth is due to the pioneering work of V.M Goldschmidt. The major separation of the different phases of the earth had occurred

OXYGEN 46.6

SILICON 27.7

other non-metals
hydrogen 0.1
phosphorous 0.1
others < 0.1

aluminium   8.3
iron   5.1
calcium   3.6
sodium   2.8
potassium   2.6
magnesium   2.1
titanium   0.4
manganese   0.1
others   > 0.1
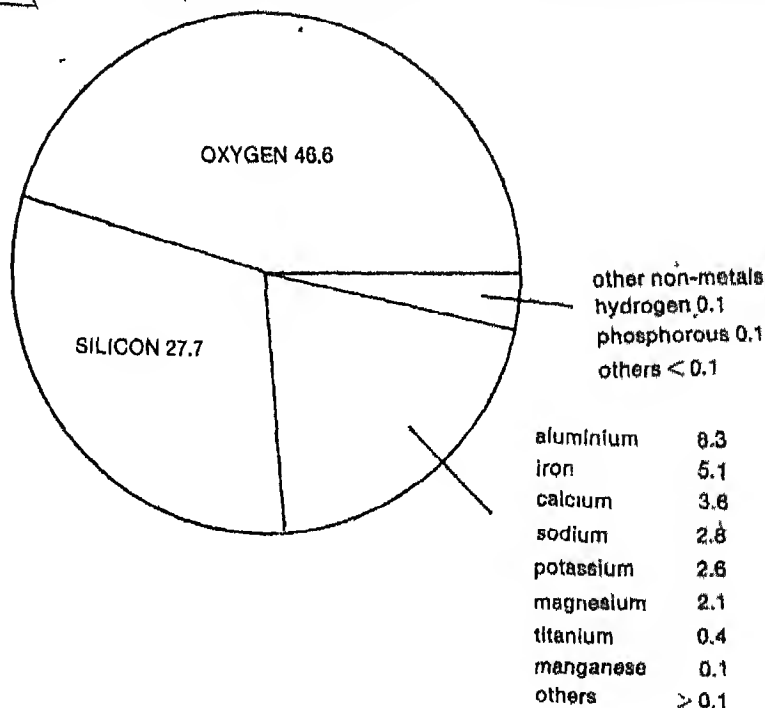
Fig. 2.1   *Percentage distribution of abundant elements in the earth's crust*

during the cooling of a gaseous mixture in the formation of the earth. In the cooling of the earth, the initial gaseous mixture condensed to a liquid. This was followed by solidification resulting in the formation of different types of rocks. The elemental composition is not the same in different rocks. Weathering of rocks over a period of time extracts some of the elements into aqueous phase leading to the formation of sedimentary rocks and sea water. The distribution of elements in a wide range of rocks found on the surface of the earth is given in Fig. 2.1. We notice that silicon and oxygen together form about 75% of the total constituents of the earth

We see from Fig. 2.1 that the familiar elements, copper, tin, mercury are less abundant. The familiarity of these elements are possibly due to their occurrence only in certain locations and their extensive usage arises from the ease of their extraction

A solid object such as the earth should consist of a core (centre portion) covered by different layers to give a particular shape. Goldschmidt suggested that the cooling of the gaseous matter resulted in major parting leading to the segregation of different zones   a metallic core, an intermediate sulphide layer, covered by a silicate crust and an atmosphere (Fig. 2.2). The presence of different layers indicates
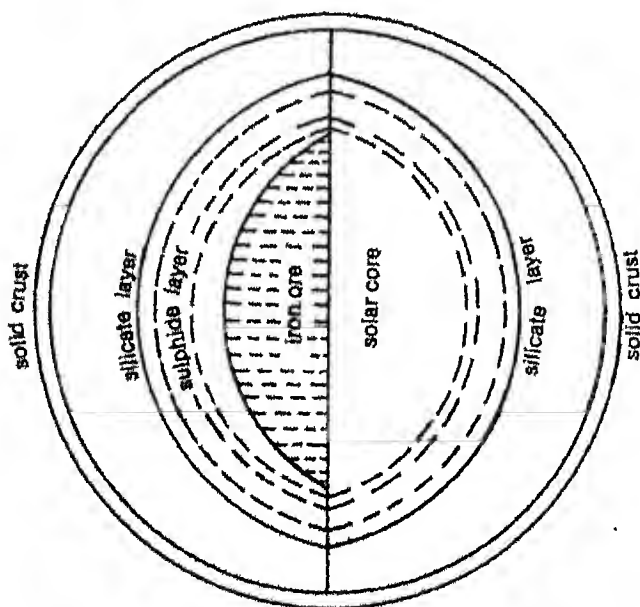
GOLDSCHMIDT   **KUHN AND RITTMAN**

Fig 2.2 *The composition of the earth according to Goldschmidt, Kuhn and Rittmann. The earth's crust is the outer layer 40 km deep. The different layers according to Goldschmdt is shown on the left side.*

concentrations of various materials in these layers that had occurred during the cooling process. The distribution of the elements in the metallic core (siderophil), sulphide zone (chalcophil), silicate crust (lithophil) and the atmosphere (atmophil) is different. The distribution of elements in the different zones is given in Table 2.2. The elemental distribution in different combinations occurring in various parts of the solid phase of the earth is due to the relative stabilities of the different materials. Many elements are present in more than one layer and this can be attributed to their easy accessibilities. There is another view. According to two Swiss scientists W. Kuhn and A. Rittmann, the core of the earth constitutes solar material containing 30% hydrogen followed by molten silicates covered with magma layer and crust.

TABLE 2 2

Distribution of Elements in Different Layers

Lithophil	Chloride, sulphate and carbonate, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba.
	Silicate and oxide, Be, Al, Si, Y, La, Ac, Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo, W, U.
Atmophil	F, Cl, Br, I, B, C, Si, N, O, He, Ne, Ar, Kr, Xe.
Siderophil (Metallic core)	Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au.
Chalcophil (Sulphide layer)	P, S, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi.

The solidification of the earth's crust is really fractional crystallisation of material over a long period of time (billions of years) to form igneous rocks. The elements that constitute these rocks are governed by the ionic size of the elements. It is natural to expect that certain ions are preferentially incorporated into silicates as aluminosilicate melts, such as Fe^{2+}, Mg^{2+}, Ca^{2+}, Na^+ and K^+. These minerals constitute four-fifths of the earth's crust.

Weathering is selective extraction of igneous rocks by water, carbon dioxide and humic acids carrying away Na^+, Ca^{2+}, Fe^{2+}, and Mg^{2+} and leaving insoluble residues, TiO_2, Fe_2O_3 and SiO_2. The differential extraction depends on the charge/size ratio of the elements. Elements, for which the ratio is less than 4 (Na^+, K^+, Mg^{2+}), are easily extracted into water (sea water). Elements for which the above ratio is greater

... ... sulphates and phosphates Elements having ... ... under reducing media and reprecipitate in oxidising media. The effect of weathering on silicate containing oxides can be visualised from the scheme depicted below. This shows the partial separation of the elements and their occurrence as carbonates, hydroxides, oxides and chlorides
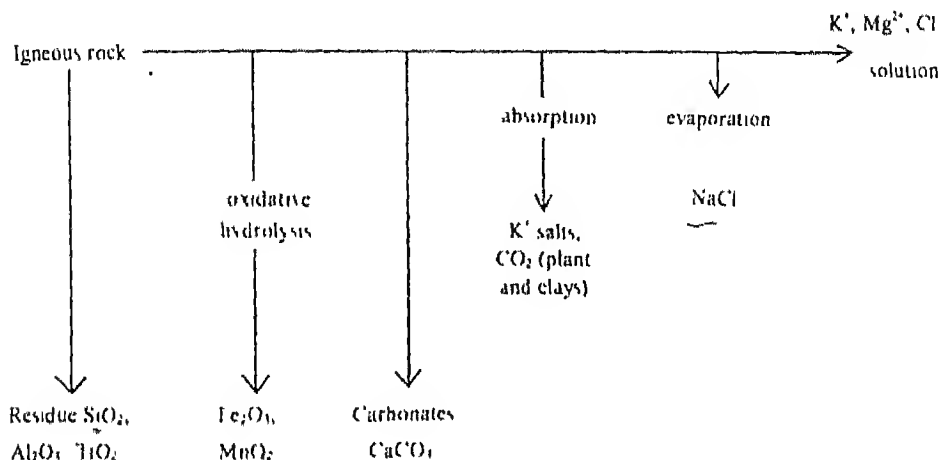
The chemical weathering process produces silica (SiO_2), alumina (Al_2O_3), iron and manganese oxides, lime and magnesia and, soda and potash. Weathering affects the nitrogen cycle and the carbon cycle.

2.2 ELEMENTS IN BIOLOGY

Many elements are accumulated in living organisms. The most familiar example is enrichment of iodine in sea weeds, vanadium in sea cucumbers and potassium in plant life. Apart from the accumulation of these elements, living organisms contain different elements concentrated in different parts (e.g., iron in hemoglobin (blood), zinc in the eyes of certain animals and magnesium in chloroplast). The chloroplasts also contain traces of manganese copper and iron. The reasons for the specific association of elements in biological functions have been little explored.

2.3 ELEMENTS IN SEA

The chemistry of the sea is largely the chemistry of complex reactions. We have learned that weathering of igneous rocks followed by extraction of elements by water is the main source of dissolved salts in sea water. These can be depicted in the following reactions sequence that occurs in the laboratory of the sea.

Igneous rock   +   Rain water ⟶ Stream water + Detritus clay

(Ca Aluminosilicate $(H_2O + CO_2)$ $(Ca^{2+}, 2K^+, 2Na^+,$ + Clay + SiO_2

$CaAl_2Si_2O_8$ + HCO_3^-)

Potassium aluminosilicate,
$KAlSi_3O_8$

Sodium alumino silicate,
$2NaAlSi_3O_8$)

Kaolinite Clay I + sea water ⟶ Clay II + H_2O + CO_2

Alumino silicate $(2K^+ + 2HCO_3^-)$ Ilite

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + H_2O + CO_2$$
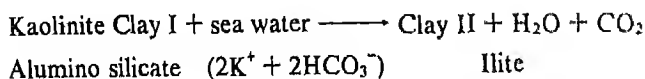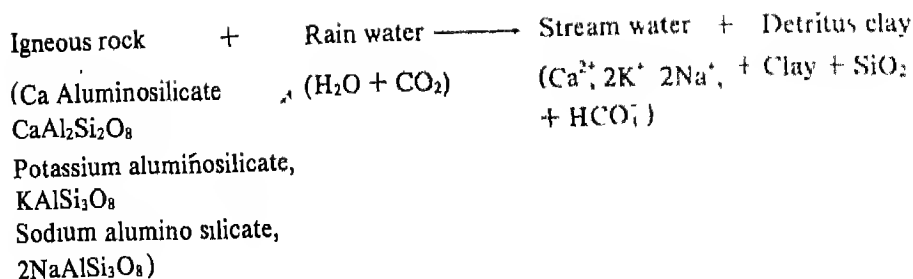
Marine organisms convert the Ca^{2+} ions to $CaCO_3$ (shells) which form sediments. HCl injected by undersea volcanoes reacts with HCO_3^- according to the equation:

$$2HCl + 2HCO_3^- \longrightarrow 2Cl^- + 2H_2O + CO_2.$$
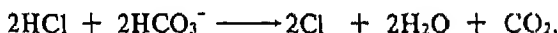
This reaction is followed by metamorphosis of clay to form Ca, K, Na aluminosilicates from igneous rocks.

Clay   +   Interstitial water $\xrightarrow[\text{pressure}]{\text{heat}}$ igneous rock + HCl + alumino silicate

$(Na^+ + Cl^-)$ $2SiO_2$

$$Na^+ + Cl^- \longrightarrow NaCl$$
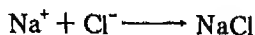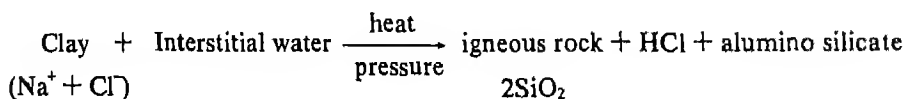
The relative composition of the elements in sea water is shown in Fig. 2.3. You may be surprised to know that only four elements, Cl, Br, Na and Mg are recovered commercially from sea water. The manganese nodules form a potential source of rare metals and it may be worthwhile extracting these elements.
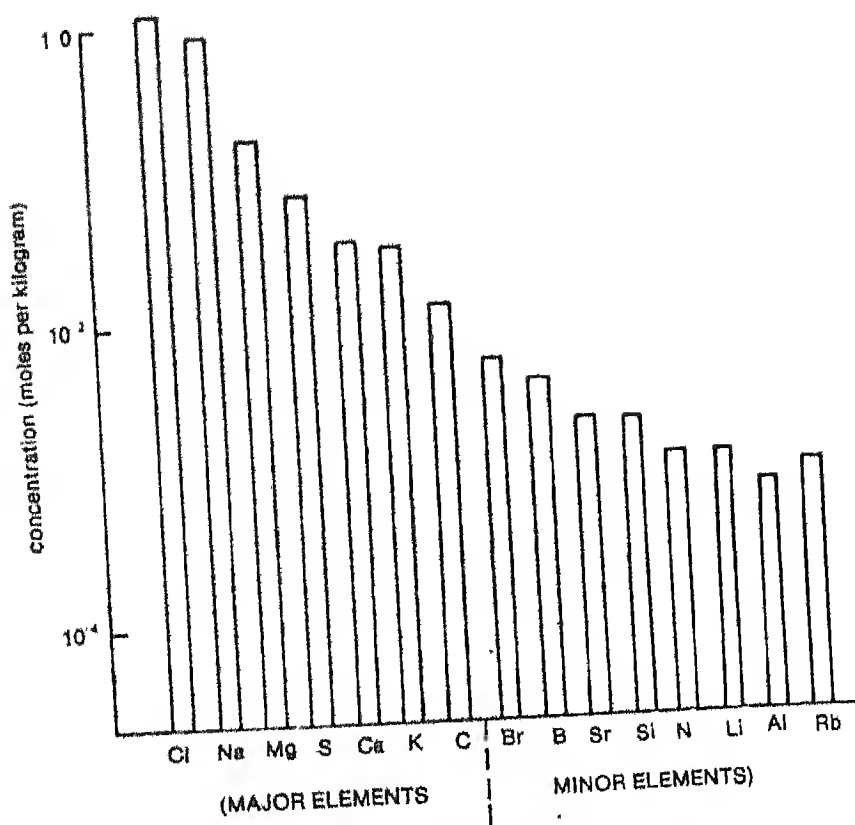
Fig. 2.3 *Elements in the Sea*

OCEANS — THE GREAT STOREHOUSE OF CHEMICALS

A largely unutilised source of food and of raw materials are the oceans of the world. The coming years are going to see increased efforts to tap this huge and in some cases a limitless reservoir of useful items.

A number of sources like rivers and volcanic eruptions are regularly dumping millions of tons of minerals and metals into the ocean. Some of these are present in the ocean in the dissolved state and some others are

deposited onto the ocean floor. A rough idea of the ocean storehouse can be obtained from the fact that the total volume occupied by the oceans is nearly 1400 million cubic kilometres with millions of tonnes of dissolved salts per cubic kilometre.

Sea-water is the leading source of bromine. Natural gas, oil, coal, sulphur, gold, and tin are amongst the items extracted commercially from the seas. The underlying ocean floor is richer in nickel, copper, and zinc than the ores on the land. Sea-weeds are an important source of inorganic and organic chemicals like Iodine, alginic acid, agar-agar and laminarin.

Pure water is obtainable from sea-water by flash distillation i.e. distillation at low pressure Unfortunately, this technique is expensive as it requires a lot of energy. It is, therefore, at present used only in countries like Kuwait and Saudi Arabia where pure water is very scarce and energy is relatively cheap.

As the demand for fresh water goes on increasing, desalination of sea-water may become an important process. At present, there are over 2000 desalination plants in operation all over the world based on techniques like flash distillation, ion exchange or reverse osmosis.

2.4 EXTRACTION OF METALS

We have learned that many elements tended to group together during the formation of the earth. These exist as deposits. The naturally occurring material in which the metals are present in stable compounds is called a MINERAL. Many minerals have the same composition as those of the compounds synthesised in the laboratory. However, the minerals are not pure. The minerals in which the metals are sufficiently concentrated and form commercial sources of desired metals are called ORES. Ores are usually associated with waste materials not useful as sources of metals. The waste material in an ore is called GANGUE The most common component of gangue is silica (SiO_2) as quartz. We shall now consider the various metallurgical processes that are employed to free metals from their ores.

2.4.1 Metallurgical Processes

The ores contain unwanted materials. The first step would be to separate the required ore from the gangue The process employed to concentrate an ore is called the beneficiation process After obtaining the concentrated ore, the desired metal is freed from other constituents of the ore. The metal obtained is often impure. The pure metal can be obtained by various processes such as electrorefining, zone refining and other methods

An outline of the various methods that are employed in the production of metals from the ores is given below:

```
                          ┌─────────────────────────┐
                          │           Ore           │
                          └─────────────────────────┘
                                     │                    Removal of gangue
                                     │
Floatation and other processes      │                    Increase of concentration of
                                     ▼                    the desired mineral
                          ┌─────────────────────────┐
                          │      Beneficiation      │
                          └─────────────────────────┘
                                     │
Leaching                             │                    Separation of other minerals
                                     ▼
                          ┌─────────────────────────┐
                          │    Concentrated ore     │
                          └─────────────────────────┘
Roasting                             │
Calcination                          │
Smelting                             │
                                     │
Reduction                            │
Chemical                             │
electrochemical                      ▼                    Removal of other elements
                                                          to obtain desired metal
                          ┌─────────────────────────┐
                          │      Impure metal       │
                          └─────────────────────────┘
Electrorefining                      │
Zone melting                         ▼                    Removal of other elements

                          ┌─────────────────────────┐
                          │        Pure metal       │
                          └─────────────────────────┘
```

In the flow diagram above, the functions of different processes are given on the right side. On the left side, the various methods that are used are denoted. There are also other methods that are not listed here. The methods are dependent on the type of

ore, the nature of the mineral chosen for metal extraction and the type of the minerals from which the mineral concentrate has to be obtained. We shall examine now the principles involved in the various methods of beneficiation of ores.

2.4.2 Production of Concentrated Ore

The first step in the beneficiation process is crushing. The crushed ore is more useful for the removal of gangue and separation of useful mineral. Generally the metal ores are heavier than the gangue. Thus by allowing the crushed ore to flow in a current of water, the lighter impurities can be washed away leaving behind heavier particles containing the minerals. This method is called LEVIGATION. A convenient method widely used in the concentration of sulphide ores is FROTH FLOATATION. The crushed pieces of minerals are denser than the water and so they sink in water. We can float a few pieces of the ore if we bubble air through the water. Some of the grains stick to the air bubble and can be brought to the surface since the average density of the bubble and the grain of the ore is less than that of water. Let us add a reagent to the water which would . . . . that more parti. . . . . This reagent is called a COLLECTOR. With the usage of different collectors, we can float minerals of the ore one after another. The floating minerals can be removed mechanically. In this manner we can obtain mineral concentrates. The gangue materials do not float and remain at the bottom of the water during these operations.

LEACHING is another process in which a particular mineral in an ore can be dissolved selectively by employing certain acids, bases or other reagents. Typically, bauxite ($Al_2O_3.2H_2O$) can be leached with sodium hydroxide solution to dissolve the alumina and the insoluble portion (unwanted material, silica and other oxides) remain as a sludge. The dissolved metal solution can be recovered by reprecipitation or crystallisation.

$$Al_2O_3 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

$$2NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3H_2O$$
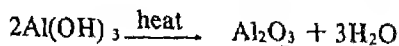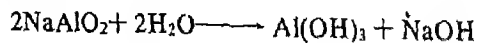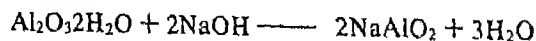
There are other separation methods for the concentration of the ores. These are based on specific properties such as gravity separation, magnetic separation, electrostatic separation and optical separation. Leaching is also employed in the recovery of some precious metals like silver and gold. It . . . . of complexation. In this process silver and gold are extracted as their cyanide complexes which are easily soluble in water.

The ores containing silver, (AgS-argentenite) and native gold are treated with an aqueous solution of sodium or potassium cyanide.

$$Ag_2S + 4NaCN \longrightarrow 2Na\,[Ag(CN)_2] + Na_2S$$

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow 4K\,[Au(CN)_2] + KOH$$
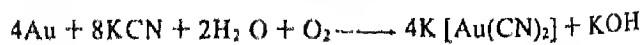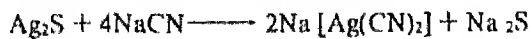
The presence of oxygen is necessary to convert gold to the oxidised state

Certain bacterial systems are known to remove specifically some metals from the ores. These can be used to selectively separate metals in low concentration.

The removal of sulphur from a few metal sulphides can be easily accomplished by heating the sulphide. This process is known as ROASTING and/or SMELTING In smelting, high temperatures are used to produce molten materials that can be reduced chemically. Sometimes, the product of such an operation could be a metal or a mixture of sulphides and metal in which the percentage of metal has been increased as a result of the smelting. This material is called MATTE.

2.4.3 Production of Metals and Their Purification

Minerals usually contain in the oxidised state (as compounds). They are associated with other impu... the production of metals are: (i) removal of impurities from the ore, and (ii) isolation of the desired metal from the minerals. The methods of removing the impurities depend on the nature of the impurities. We have learnt that one of the most abundant impurities is silica, SiO_2 and oxides of phosphorus. These are removed by converting them to molten silicates or phosphates of calcium. This is carried out by heating these oxides in the presence of calcium oxide.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

$$P_4O_{10} + 6CaO \longrightarrow 2Ca_3(PO_4)_3$$
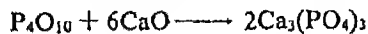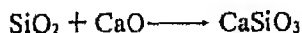
The molten silicates and phosphates can be easily removed from the solid metal compounds. The removal of impurities from a mineral by forming molten salts is called SLAGGING OPERATION. The slag consists of the molten impurities, generally as a metal silicate.

Metals in the minerals are present as oxides, carbonates or sulphides (Table 2.1). In order to obtain metals, we have to free them from their compounds. In other words, we have to reduce the metals from their oxidised state to the metals. There are two methods of doing this—chemical reduction and electrolytic reduction. First, it is necessary to convert metals into their respective oxides or sulphides. Hence the minerals containing as carbonate or a hydroxide are converted into

oxides by heating them strongly so as to remove any volatile impurities. This process is called CALCINATION. A few examples are:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$Cu_2CO_3(OH)_2 \longrightarrow 2CuO + H_2O + CO_2$$

$$CaCO_3 \cdot MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$
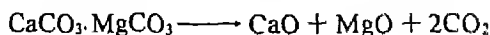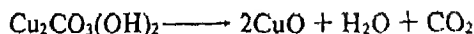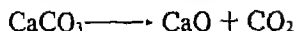
(Dolomite)

The sulphide minerals are converted into oxides by a process called ROASTING. In this process, the sulphide ores are heated in a controlled atmosphere of air so as to remove the volatile sulphur and other impurities as oxides; the desired metal oxides are left behind. Some examples are given below:

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$
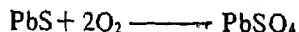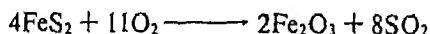
In the above example, you will notice that lead sulphide can be converted to lead sulphate

Reduction

After obtaining metal oxides or sulphides in a pure form, the metals can be obtained by reduction. The principle of this method is to remove the oxygen of the metal oxides by treating them with carbon, carbon monoxide or another element for which oxygen has greater affinity and forms a more stable oxide. In the electrolytic method, the electrons serve as a reducing agent to convert the metal oxides to metals. The mineral electrolyte should be in the molten state and therefore molten oxides and halides are employed. The choice of the method, whether to use a chemical or an electrolytic process, depends on various factors. For example, some metal oxides such as Al_2O_3 are _____ ___ _ ____ _ _ ___ _ __ _ __ __ __ agents. In such cases, we have to employ the ___ ___ __ ____ ___ __ _ _ _ __ __ reducing agent employed in the chemical reduction method depends on the chemical reactivities of the metal. The earliest known method of extraction of metals makes use of hot charcoal. Combustion of charcoal leads to the formation of carbon monoxide. Both carbon and carbon monoxide are reducing agents capable of reducing the metal oxides to metal. A few examples are given below:

$$ZnO + C \longrightarrow Zn + CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

A simple experiment in the laboratory could be used for the reduction of metal oxide by hot charcoal. Take a charcoal piece and scratch out a small piece from the surface of the charcoal. Place an oxide of metal (above example) in the charcoal. With the help of a blow pipe direct the flame of the burner on to the oxide holding the charcoal with a pair of tongs. You can observe the metallic lustre of the residue of the metal oxide. Can we use methane gas for reduction of a metal oxide?

In some cases, we can obtain the metal from the metal oxide by heating the oxide with another metal. One such important process involves the reduction of metal oxides (Fe_2O_3, Cr_2O_3) by aluminium. This process is known as ALUMINO-THERMIC PROCESS. These reactions liberate a large amount of heat. The metals are obtained in the molten state and hence can be easily separated from the products of the reaction. A few examples are

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$$

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
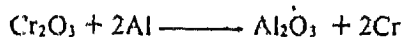
The metal magnesium can also be employed. For example titanium could be obtained from titanium tetrachloride using magnesium metal.

$$TiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Ti$$

In certain cases, heating or roasting leads of the formation of metal.

Interestingly, some sulphides could be used for the reduction of oxide. A typcial example is the production of copper from copper pyrites. The process employed here is smelting. The copper ore containing copper pyrites ($CuFeS_2$) can be concentrated by the floatation process. On smelting, the following reactions occur:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

A few metal oxides are thermally unstable.

Electrolytic Reduction
Metals which are highly reactive can be obtained by electrolytic reduction. Some of the metals obtained by the electrolytic reduction method are sodium, magnesium and aluminium. Since these metals are highly reactive, we must protect these metals after the formation in the electrolysis, or we remove them for the

electrolyte after their formation to avoid further reaction. The electrodes employed for electrolysis should be inert

After obtaining the metal by the processes of reduction, it is further refined to get pure metal. Some of the processes are electrolytic refining, zone refining, etc. In the electrolytic process, the impure metal forms the anode and pure metal in the form of sheets or rods forms the cathode. The passage of an electric current through the electrolytic solution (or molten salt), results in the dissolution of impurities from the anode and these collect as a muddy deposit. The pure metal gets deposited on the cathode.

Some metals are required in very high purities for specific applications. Typically high purity silicon and germanium are used as semi-conductor materials. Purification of such materials are often carried out by the ZONE REFINING METHOD

In this process, an impure metal rod is taken and heat is applied at a narrow region By slowly moving the heat source, the molten region is gradually transferred from one end of the rod to another. The impurities which remain in the molten part are progressively shifted to one end of the rod. The process could be repeated many times till the desired level of purity is attained

2 5   MINERAL WEALTH OF INDIA

India is quite rich in a variety of minerals. Bihar and Orissa have large deposits of ores of iron, manganese, copper, chromium in addition to coal, mica and phosphates. Karnataka has gold in addition to iron and chromium ores. Madhya Pradesh has sizeable reserves of iron and manganese ores, limestone, bauxite and coal. Rajasthan is rich in non-ferrous metals like copper, lead and zinc in addition to mica and beryllium. Tamil Nadu has sizeable deposits of iron, manganese ores, magnesite, mica, limestone and lignite. There are many industries in India producing metals like iron, aluminium, gold, zinc, etc.

2.6   QUALITATIVE TESTS OF METALS

Qualitative analysis of metals deals with the detection of metals in compounds or mixtures of compounds. We have seen that the extraction and purification of metals involve a variety of chemical reactions. These reactions depend on the nature of the metal and the nature of the metal salt. The detection and identification of metal are important in the metal extraction and purification procedures.

The preliminary aids for qualitative analysis are the appearance (colour) and the solubility characteristics. The colour of metal compounds provides the first clue to the nature of the metal. For example, compounds of chromium iron, cobalt, copper, nickel, etc, are coloured, while compounds of aluminium, sodium, magnesium are colourless. Further, the colour of a metal compound indicates its nature. For example, copper carbonate is green; copper sulphide is black; manganese dioxide is

black; and manganese sulphate is pink.

The solubility of metal compounds in an aqueous medium is an important feature of qualitative analysis. Usually, the analysis starts with the dissolution of the material in a suitable medium and precipitation of the metal to be analysed as an insoluble salt. One of the useful ways of obtaining a solution of the material to be analysed is to dissolve it in hydrochloric acid or in an oxidising acid solution. Some metal oxides such as titanium oxide and silica, are quite inert. In these instances one has to employ fusion of these oxides with sodium carbonate or peroxide to bring them into solution. The solubility of metal salts in water depends on the charge to size, ratio of the metal ions and also on the nature of the salt such as nitrate, sulphate, oxides, sulphides, etc. Table 2.3 shows the solubility of a few metal salts in water.

TABLE 2.3

Solubility in Water of a Few Metal Salts

Salt	Metals forming soluble compounds	Metals forming insoluble compounds
Oxide/hydroxide	Na^+, K^+, Ba^{2+}	Most of the other metals
Sulphides	Na^+, K^+	Mg^{2+}, Ca^{2+}, BaS, Al^{3+}, most of the metals
Carbonates	Na^+, K^+	Most of the metals
Sulphates	Most of the metals	Ba^{2+}, Pb^{2+}, Ca^{2+} and Ag^+ slightly soluble
Nitrates	All	
Chlorides	Most of the metals	Ag^+, Pb^{2+}

In qualitative analysis, a careful application of solubility characteristics of metal ions is employed to separate metals from one another and to identify them. The identification of a metal is often carried out by forming a specific compound of the metal which is usually coloured.

Let us consider an example to illustrate the above point. Copper occurs as malachite green mineral. This is sparingly soluble in water. On addition of an acid, we notice the evolution of a gas. The gas turns lime water milky. Hence we identify the salt as a carbonate. The acid solution containing copper ions can be precipitated as black sulphide by passing hydrogen sulphide gas. Therefore, we identify the malachite green as copper carbonate. You will learn more about these aspects in your practical classes.

EXERCISES

2 1   The geological processes involved in the distribution of elements in specific regions of the earth are solubility in aqueous solution, density, melting point and chemical reactivity. Among these processes which are the ones responsible for (i) the formation of igneous rocks containing minerals, and (ii) occurrence in the native state?

2.2   Describe the methods generally used to extract metals.

2.3   What are the different methods used to obtain concentrated ores?

2 4   Name the sulphide ores for tin, lead, copper, silver and silver metals

2.5   Name the oxide ores of iron, zinc, aluminium and manganese

2 6   Silver ores and native gold have to be leached with metal cyanides. Suggest a reason for this.

2 7   Describe the methods used for refining metals.

2 8   From the table on solubility of metal salts in water identify.
   (i)   Which barium salt is insoluble?
   (ii) Which lead salt is soluble?
   (iii) Which hydroxide is insoluble?
   (iv) Which iron salts are soluble?

U N I T 3

STATES OF MATTER

If I were in the world of molecules I would rather be in the liquid state, with some freedom of gases and some order of solids.

OBJECTIVES

In this Unit, we shall learn

* the gas laws (Boyle's law, Charles' law, Dalton's law of partial pressure and equation of state for an ideal gas);

* to carry out calculations based on the gas laws;

* to interpret the gas laws on the basis of kinetic-molecular model of a gas;

* the general characteristics, classification and structure of solid.

* the properties of liquids.

THE CHEMICAL CLASSIFICATION of matter into elements, compounds, and mixtures was discussed in Unit 1 We now take up the physical classification which separates all matter into three categories—solids, liquids, and gases known as the three states of matter This classification is more obvious since we are familiar with solid water (ice), liquid water, and gaseous water (steam). Almost all the substances exist in the three states under appropriate conditions of temperature and pressure.

Many properties of solids, liquids, and gases can be easily observed with our unaided senses * For example, a solid has a definite size and shape which do not depend on the size and shape of the container The shape of a solid can be changed but it usually requires considerable force. Contrast this with the behaviour of a gas which has neither definite shape nor definite vloume; a gas flows and expands to fill any container in which it is placed A gas is easy to compress Liquids show an intermediate behaviour. A liquid flows and assumes the shape of the container but it does not expand to fill the container A liquid is only slightly compressible. A liquid has a much higher density than a gas but a smaller density than a solid.

The above description is based on everyday observations with the unaided senses. Such a description is called a macroscopic description. The behaviour of the three states of matter in terms of the atomic theory is called a microscopic description since atoms cannot be directly observed. One of the objectives of chemistry is to explain the macroscopic behaviour in terms of the microscopic description. We will do this as we discuss each of the states in greater detail.

3.1 THE GASEOUS STATE

In addition to the properties described above, gases are characterised by certain quantitative relationship between mass, pressure, volume, and temperature. It will be useful to examine first how some of the gaseous properties are measured and then see the interrelationship between them.

3.1.1 Measurable Properties of Gases

The important properties are: (i) mass, (ii) volume, (iii) pressure, and (iv) temperature.

Mass: The mass of a gas can be determined by weighing a container in which the gas in enclosed and weighing the container' again after removing all the gas. The difference between the two weights gives the mass of the gas. The mass is related to the number of moles by the equation,

---

* We have five sensory organs which act like five 'windows' to the world. These are: eyes (sight), ears (hearing), nose (smell), tongue (taste), and skin (touch). In ordinary, everyday situations we use them as such, i.e., we rely on unaided senses. We can extend the range and capacity of these senses by using special types of instruments. For example, a-microscope and a telescope enable us to see many details which are invisible to the naked eyes

$$n \text{ (number of moles)} = \frac{m \text{ (mass in grams)}}{M \text{ (molar mass)}}$$

We recollect here that 1 mole of a substance contains 6.02×10^{23} molecules

---

In the SI units, volume is measured in cubic metre; one cubic metre (1 m^3) is the volume of a cube of 1 m length. For many chemical measurements, this unit is too large. The smaller unit cubic decimeter (dm^3) or cubic centimetre (cm^3) are therefore introduced. The conversion factors are:

$$1 \ m^3 = 10^3 dm^3 = 10^6 \ cm^3$$

However, the units of litre (L) and millilitre (ml) continue to be commonly used to measure volumes of liquids and solutions. Originally, a litre was defined as the volume of 1 kg of water at $3.98°C$ (where water has maximum density) but it has now been redefined as exactly one-thousandths part of a cubic metre i.e. one litre is exactly equal to one cubic decimetre (dm^3). If follows that one millilitre is equal to one cubic centimetre (cm^3). In other words, litre and dm^3 are equivalent units and so are millilitre and cm^3.

Volume: The volume of a substance is the space occupied by the substance. Since gases occupy the entire space available to them, the measurement of volume of a gas only requires a measurement of the volume of the container confining the gas.

Generally, the volume is specifed in units of litre (L), or cubic metre (m^3) or cm^3 or dm^3 As the name implies, 1 cm^3 is the volume of a cube of 1 cm length, 1 cm breadth and 1 cm height. Note the following relations between different units.

$$1 \ L = 1 \ dm^3$$
$$1 \ dm^3 = 10^3 cm^3$$
$$1 \ m^3 = 10^3 dm^3$$

Pressure: Pressure is force per unit area. A confined gas exerts uniform pressure on the walls of its container in all directions

A convenient method for measuring atmospheric pressure utilises a device known as a mercury barometer (Fig 3.1). A barometer can be made by filling mercury in a long tube (longer than 76 cm) closed at one end and inverting the tube in an open vessel of mercury. The mercury level in the tube drops until the mercury column exerts a downward pressure on the mercury in the open vessel which is exactly balanced by the atmospheric pressure. Under these conditions, the mercury in the tube falls to a height approximately 76 cm above the level of the mercury in the open vessel. When the atmospheric pressure increases, the height of the mercury column rises; when the pressure of the atmosphere decreases, the height of the column decreases.
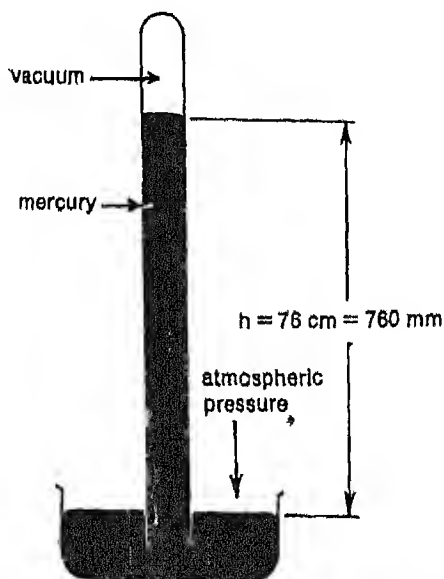
Fig. 3.1 *A mercury barometer. The pressure of atmosphere is equal to the pressure of the mercury column At standard atmospheric pressure and at a temperature of 273 K, the height of the mercury column is 76 cm or 760 mm*

The pressure expressed in terms of the height of the mercury column can be converted into units of force per unit area. A mercury column h cm high and A cm^2 in cross-section exerts a downward force equal to the weight of the mercury column. Let the force on unit area of surface be given by P.

$$P = \frac{Force}{Area} = \frac{Mass \times Acceleration}{A} = \frac{mg}{A}$$

where m is the mass of the mercury in the tube and g the acceleration due to gravity. If the density (i.e., mass per unit volume) of mercury is ρ, then the mass of the mercury in the tube is equal to ρV, where V is the volume of the mercury in the tube. Since the volume is given by Ah, we have

$$P = mg/A = \rho Vg/A = \rho Ahg/A = \rho hg$$

By international agreement, a standard pressure of one atmosphere (1 atm) is defined as the pressure exerted by exactly 76 cm of mercury at 0°C (density, 13.596 g/cm³) and at standard gravity 9.81 ms⁻²

Further, 1 atm = 76.0 cm of mercury

= 760 mm of mercury

The SI unit of pressure is a pascal defined as the pressure exerted when a force of 1 newton (1N) acts on an 1 m² area. The relation between the two units is

1 atm = 101.325 kPa

For approximate work, one atmosphere can be taken to be 10^2 kPa or 10^5 Pa

Temperature· The measurement of temperature is based[*] on the fact that many substances expand on increasing the temperature. Expansion of mercury is commonly made use of to measure temperature. In the celsius scale (formerly known as the centigrade scale), the freezing point of water (0°C) and the boiling point of water (100°C) at one atmosphere pressure are taken as reference points and this range is divided into one hundred equal parts. Thus each division corresponds to 1°C Since the zero in the celsius scale is arbitrarily fixed it is possible to have negative temperature on the celsius scale corresponding to the temperature below the freezing point of water. It may appear that the celsius scale can be indefinitely extended to negative temperatures, but experimental behaviour of gases shows that temperatures below---273.15°C are impossible to attain. This fact has led to the formulation of the absolute scale of temperature which we will discuss in section 3.1.3.

3.1.2 Boyle's Law

The first set of quantitative mesurements on the gaseous state were made by Robert Boyle in 1662. He devised a very simple apparatus to study the relation between pressure and volume of a gas. Using a bent tube and some liquid mercury, Boyle found that the length of the trapped air (to which the volume of the air was directly proportional) varied inversely with pressure applied to it (Fig.3.2). Boyle performed the experiment in a room where the temperature was approximately constant and he
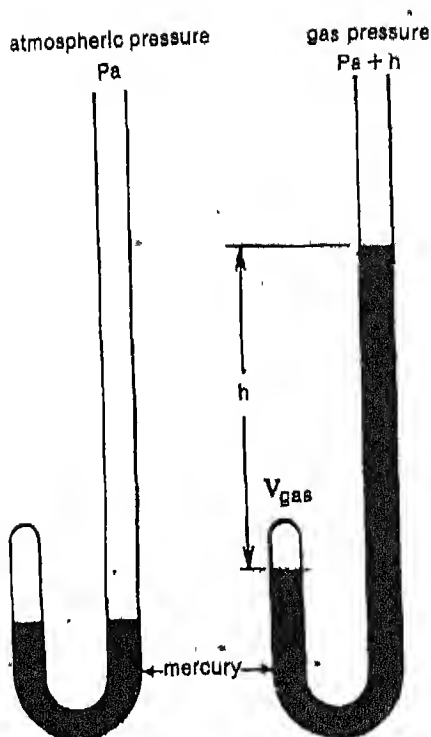
Fig. 3.2 *The simple J-tube apparatus used by Boyle to measure pressure and volume. In (a) the gas pressure is equal to the atmospheric pressure whereas in (b) the gas pressure is equal to h + P$_a$ where P$_a$ is the atmospheric pressure.*

only needed a bent tube, some mercury, and a measuring scale for his experiment. Boyle worked only with air, but when other gases were discovered, it was found that they also showed the same relationship between volume and pressure at constant temperature A sample of experimental data are given in Table 3.1 , and some plots of the data are shown in Fig 3 3

The inverse proportionality between volume (V) of a *given mass* of gass and pressure (P) applied on it, keeping *temperature constant,* is expressed by the equation

$$V \propto \frac{1}{P}$$ (Temperature and amount of gas being held constant)

or V = Constant/P

or PV = Constant

TABLE 3 1

Effect of Pressure on the Volume of a Gas (Air) at Constant Temperature

Pressure, P (atm)	Volume, V (litre)	PV (litre atm)
0.20	112.0	22.4
0.25	89.2	22 3
0.35	64.2	22 47
0.40	56 25	22.50
0.60	37.40	22 44
0.80	28 1	22 48
1 00	22 4	22.40

The last equation states Boyle's law as:

The product of pressure and volume is constant for a given amount of a gas at a constant temperature.
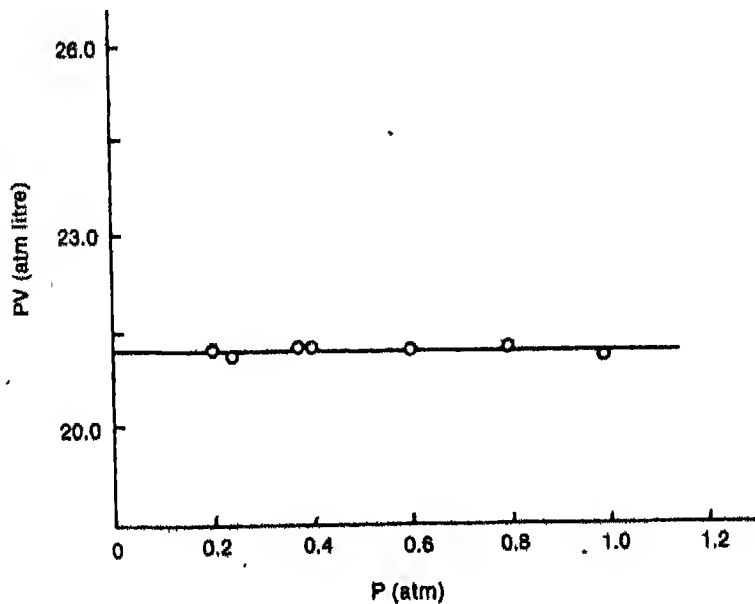
Fig. 3.3a   *Depicting Boyle's Law (plot of PV versus P)*
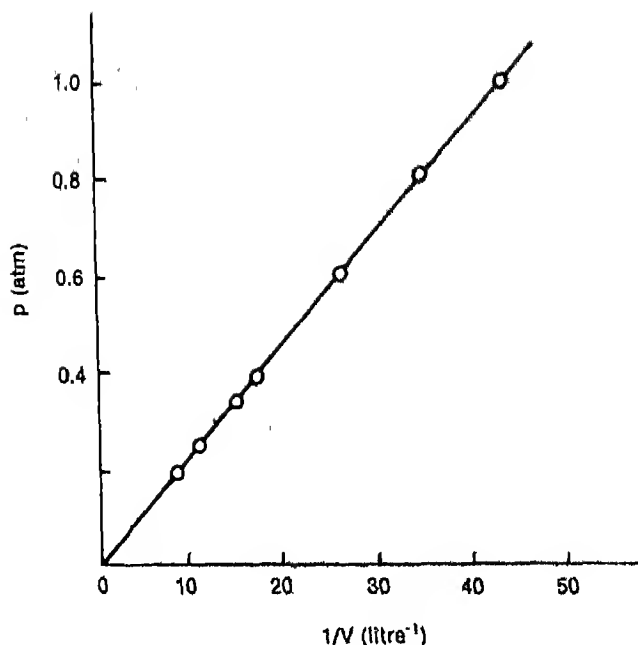
Fig. 3.3(b)   *Depicting Boyle's Law (plot of P versus $\frac{1}{V}$)*

A convenient form of Boyle's law equation is:

$$P_1 V_1 = P_2 V_2 \text{ (Amount and temperature constant)}$$

Where P_1 is the initial pressure, V_1 is the initial volume, P_2 is the final pressure and V_2 is the final volume. This equation between four variables (i.e., P_1, V_1, P_2 and V_2) is useful for calculations as it means that if any three variables are known, the fourth one can be determined.

What are the practical implications of Boyle's law? The law expresses in a quantitative manner the important experimental fact that gases are compressible. When a given mass of gas is compressed, the same number of molecules occupy a smaller space. This means that the gas becomes denser. For example, air at sea level is dense because it is compressed by the mass of air above it. However, the density and the pressure decrease with increase in altitude. The atmospheric pressure at Mount Everest—the highest peak in the world—is only about 0.5 atm, causing the air at this height to be much less dense than at sea level. The decrease in the oxygen pressure at high altitudes causes altitude sickness (sluggish feeling, headache) due to decrease in the oxygen intake in each breath. Mountain climbers and the jawans guarding our frontiers in Ladakh, undergo extensive training to adapt their bodies

to the low oxygen pressure; they also carry oxygen cylinders for an emergency. Similarly, the interiors of jet airplanes, which normally fly at about 10,000 m, are specially maintained at normal pressure and they are also equipped with emergency oxygen supply in case the pressure falls.

Example 3 1

What is the volume of a sample of oxygen at a pressure of 2.50 atm, if its volume is 3.15 l at 1 00 atm?

Solution

Let

$$P_1 = 1.00 \text{ atm} \qquad V_1 = 3 15 \text{ L}$$
$$P_2 = 2 50 \text{ atm} \qquad V_2 = \text{To be determined}$$

From Boyle's Law

$$P_1V_1 = P_2V_2$$
$$\text{or} \qquad V_2 = P_1V_1/P_2$$

Substituting the values, we get

$$V_2 = \frac{1 00 \text{ atm} \times 3.15 \text{ L}}{2.50 \text{ atm}} = 1.26 \text{ L}$$

Hence, the sample of oxygen occupies 1.26 L. at 2.50 atm. This makes sense since as the pressure increases, the volume must decrease.

3.1.3 Charles' Law and Absolute Scale of Temperature

If you take a balloon filled with air, it will expand when placed in warm water and contract in cold water. The variation in volume of a gas with temperature is thus easily observable (see Fig.3.4). A careful study of this phenomenon was first carried out by the French chemist, Jacques Charles, in 1787 and then extended in 1802 by
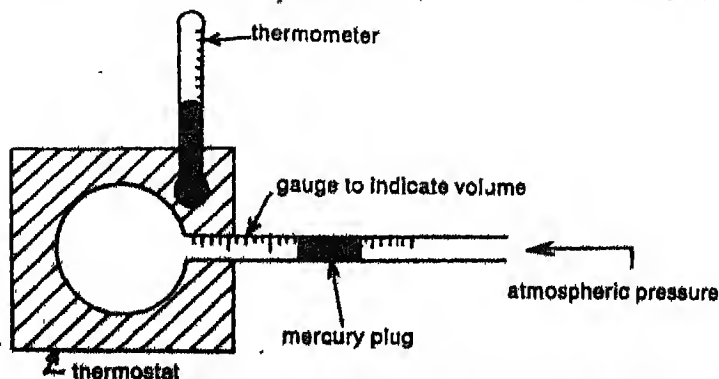
Fig. 3.4 *Apparatus for demonstrating the effect of temperature on the volume of a gas at constant pressure. The gas in the flask can be heated or cooled at constant (atmospheric) pressure. The mercury plug moves back and forth depending on the volume of the gas.*

another French chemist, Joseph Gay-Lussac. They found that air (or any other gas) expands when heated. If the pressure is held constant, the ratio of the volume (V_2) of a given mass of air at 100^0C to its volume (V_1) at 0^0C is constant and it is independent of the initial volume. Experiments show that this ratio is 1.366, i.e.,

$$V_2/V_1 = 1.366$$

or $$V_2 = 1.366\ V_1 = V_1(1 + 0.366)$$

or $$V_2 = V_1 + 0.366\ V_1$$

This equation means that the volume of the gas at 100^0C is greater than its volume at 0^0C by 0.366 times its volume at 0^0C. Since this expansion is for 100^0
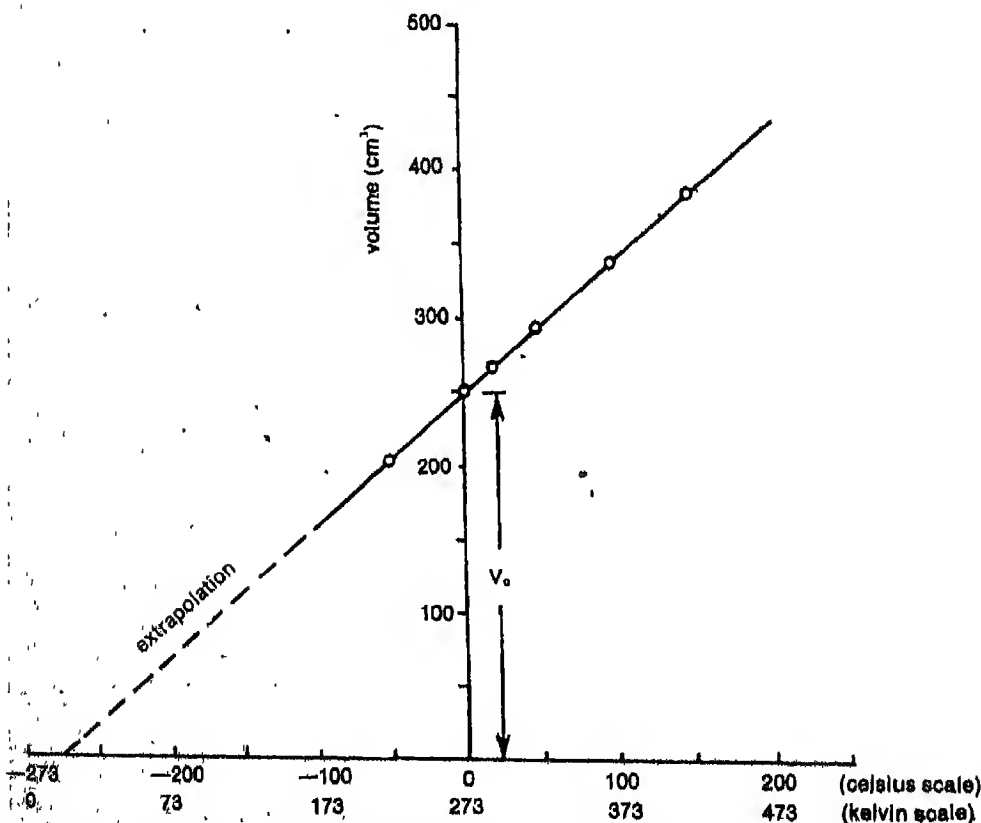
Fig. 3.5 *A plot of volume versus temperature data (Table 3.2) shows that at constant pressure, volume V and temperature, t obey the linear equation V= mt + C.* Extrapolation of the line to zero volume indicates that − 273^0C is the lowest temperature possible

change in temperature and since the expansion is found to be uniform, it follows that the expansion *per unit degree* will be by $(0.366/100)$ V_1 or $(1/273)$ V_1. In other words, for every 1 change in temperature, the volume of a gas changes by $1/273$ of its volume at $0°C$. The experiments thus establish that the volume of a gas is a linear function of its celsius temperature (Fig 3.5)

Absolute scale of temperature. The fact that the volume of a gas decreases with the temperature, raises an obvious question. Is it possible to lower the temperature of a gas so much that its volume becomes zero? We know that the volume decreases by $1/273$ of its volume at 0 for a fall in temperature. The volume must thus be reduced to zero and thus at $-273°C$. Any further lowering is impossible since it would imply negative volumes — a meaningless concept. We thus arrive at the interesting conclusion that $-273°C$ is the lowest possible temperature. It would be logical to call this the ABSOLUTE ZERO OF TEMPERATURE. A scale of temperature based on this choice of zero is known as the ABSOLUTE SCALE OF TEMPERATURE. Since this scale was first suggested by the British scientist Lord Kelvin, it is also known as the KELVIN SCALE.

Careful measurements show that the absolute zero of temperature is $-273.15°C$. Temperatures on the Kelvin scale are indicated simply by writing the letter K; by convention, the degree sign (°) is not used when expressing temperatures on the Kelvin scale. Thus,

$$-273.15°C = 0 \text{ K}$$

The relation between the Kelvin scale and the Celsius scale is

$$T = t + 273.15$$

Where T is the temperature on the Kelvin scale and t is the temperature on the Celsius scale. In short, temperature on the Kelvin scale is obtained by adding 273.15 (or less accurately by adding 273) to the temperature on the Celsius scale.

It should be noted that our conclusion that gases should occupy zero volume at 0 K cannot be verified in practice since all gases condense to liquids and solids before this temperature is reached. Nevertheless, the concept of absolute zero is very important as it gives rise to the absolute scale of temperature. This scale, basic to all scientific work, can be justified by thermodynamic arguments. In fact, the Kelvin scale is also known as the THERMODYNAMIC SCALE OF TEMPERATURE. Since many equations assume a simple form (an example is Charles' law given below) on this scale, the Kelvin scale is used in all scientific work.

Charles' Law: The volume of a gas is a linear function of the temperature on the Celsius scale but it turns out that the volume is *directly* proportional to temperature
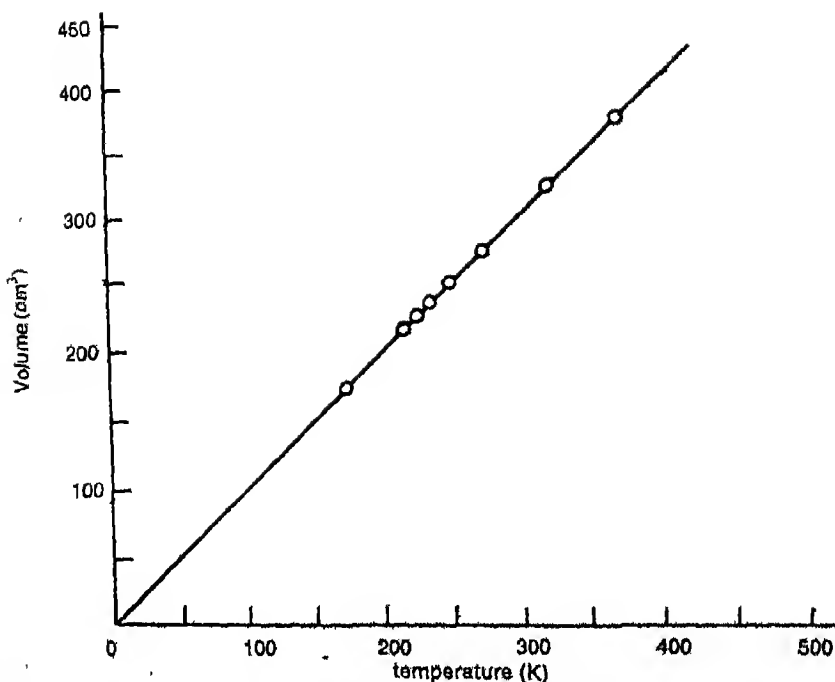
Fig. 3.6 *Another plot of data of Table 3.2 shows that volume is directly proportional to the absolute temperature*

(pressure maintained constant), if the temperature is expressed on the Kelvin scale (Fig 3.6) i.e.,

   $V \propto T$
   or $V = $ constant $\times$ T   (Pressure and amount of gas being held constant)
   or $V/T = $ constant

Charles' law is commonly stated as:
   The volume of a given mass of a gas is proportional to the temperature on the Kelvin scale at constant pressure.
   A convenient form of Charles' law equation is:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \text{ (amount and pressure constant)}$$

Where V_1 is the initial volume, T_1 is the initial temperature, V_2 is the final volume and T_2 is the final temperature. This equation between four variables (i.e., V_1, V_2 T_1

TABLE 3.2

Changes in the Volume of a Fixed Mass of a Gas with the Temperature (Pressure Remains Constant)

Temperautre		Volume	Temperature		Volume
C	K	cm³	C	K	cm³
− 50	223	223	50	323	323
0	273	273	100	373	373
10	283	283	150	423	423

and T_2) is useful for calculations as it means that if any three variables are known, the fourth one can be determined.

The use of hot-air balloons in sports and for meteorological observations is an interesting application of Charles' law. Since gases expand on heating, hot air is less dense. This causes a hot-air balloon to rise by displacing the cooler (and hence denser) air of the atmosphere. In the 1930s, hydrogen ballons (which rise higher because of the lower density of hydrogen) were developed as a means of transportation across the Atlantic. However, such airships were risky due to the inflammable nature of hydrogen In fact, the German airship *Hindenburg* was destroyed by fire in 1937 which led to the end of airship as public transport but hydrogen balloons and hot-air ballons continue to be used for weather observation.

Example 3.2

A sample of hydrogen gas is found to occupy 906 cm³ of volume at 300 K (i e., 27°C). Calculate the temperature at which it will occupy 500 cm³ of volume

Solution

Let

$$V_1 = 906 \text{ cm}^3 \qquad\qquad T_1 = 300 \text{ K}$$

$$V_2 = 500 \text{ cm}^3 \qquad\qquad T_2 = \text{To be determined}$$

From Charles' Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or

$$T_2 = \frac{V_2 \times T_1}{V_1}$$

Substituting the values, we get

$$T_2 = \frac{500\ cm^3 \times 300K}{906\ cm^3} = 165\ K$$

$$= 165\ K\ (or - 108°C)$$

The result is easy to understand because a gas occupies a smaller volume at a

lower temperature.

3 1.4 Avogadro's Hypothesis

You have learnt in Section 1.4 that Amedeo Avogadro (1811) proposed the following hypothesis: Equal volumes of all gases contain equal number of molecules under the same conditions of temperature and pressure. This implies that volume is proportional to the number of molecules. From the definition of a mole (See Section 1.4.1), it follows, that the amount of any gas can be stated in moles and that one mole of any gas contains the same number (6.02×10^{23}) of molecules In terms of moles, Avogadro's hypothesis may be expressed as equal volumes of gases contain the same number of moles, or volume is directly proportional to the number of moles. In equation form,

Volume = Constant $\times$ Number of Moles
(Temperature and pressure held constant)

3.1.5 Ideal Gas Equation

In order to see how Boyle's law, Charles' law and Avogadro's hypothesis can be combined, let us consider a quantity of gas occupying volume V_1 at temperature T_1 and pressure P_1 and ask the question what volume this gas will occupy at some different pressure P_2 and temperature T_2. This change in volume can be carried out in two steps

$$P_1V_1T_1 \xrightarrow{\ Step\ I\ } P_2V_xT_1 \xrightarrow{\ Step\ II\ } P_2V_2T_2$$
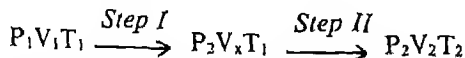
In the first step (T constant), Boyle's law (i.e., $P_1V_1 = P_2V_x$) can be used to obtain

$$V_x = (P_1V_1)/P_2$$

In the second step (P constant), Charles' law (i.e., $V_x/T_1 = V_2/T_2$) can be used to obtain

$$V_x = (V_2T_1)/T_2$$

Combining the two expressions for V_x, we get

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2}$$

$$\text{or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This equation between six variables (i.e., P_1, V_1, T_1, P_2, V_2 and T_2) is very useful for calculating the value of one of the variables if the other five are known.

The above equation also implies that the ratio of PV to the absolute temperature T is constant for a given quantity of any gas. We may state it in equation form as, $(PV/T) = K$, a constant depending upon the amount of the gas. To make this equation independent of the amount of a gas, we use the fact that the volume of a gas at constant temperature and pressure is directly proportional to the number of moles (see Section 3.1.4). This means that K is directly proportional to the number of moles, n, i.e.,

$$K \propto n$$

$$\text{or } K = nR$$

Where R is a constant of proportionality *independent* of the amount of the gas. It follows that

$$PV/T = nR$$

$$\text{or } PV = nRT$$

which is called the IDEAL GAS EQUATION. The constant R has the value of PV/T for one mole of gas and is the same for all gases and is known as the universal gas constant.

Example 3.3

A sample of nitrogen gas occupies 320 cm^3 at standard temperature and pressure (i.e., at 273 K and 1.00 atm). Calculate its volume, when the temperature is 66°C and pressure is 0.825 atm.

Solution

We are given

$P_1 = 1.00$ atm	$P_2 = 0.825$ atm
$T_1 = 273$ K	$T_2 = 339$ K
$V_1 = 320$ cm^3	$V_2 =$ To be determined

Since temperature and pressure are both changing, it is necessary to use the combined gas law, i e.

$$\frac{(P_1 V_1)}{T_1} = \frac{(P_2 V_2)}{T_2}$$

$$V_2 = \frac{(P_1 V_1 T_2)}{(P_2 T_1)}$$

Substituting the values, we get

$$V_2 = (1.00 \text{ atm} \times 320 \text{ cm}^3 \times 339K) / (0.825 \text{ atm} \times 273K)$$

$$= 482 \text{ cm}^3$$

The Gas Constant.   Rearranging the equation of state, we find that $R = PV/nT$ The value of R is the value of PV/T for one mole of a gas. Since one mole of a gas is found to occupy a volume of 22.414 litres at 1 atmosphere pressure and 273.15K, we get

$$R = \frac{PV}{nT} = \frac{1.00 \text{ atm} \times 22.414 \text{ litre}}{1.00 \text{ mol} \times 273.15 \text{ K}}$$

$$= 0.0821 \frac{\text{litre atm}}{\text{mol K}}$$

If the pressure is written as force per unit area and the volume as area times length we have

$$R = \frac{\dfrac{\text{FORCE}}{\text{AREA}} \times \text{AREA} \times \text{LENGTH}}{n \times T} = \frac{\text{FORCE} \times \text{LENGTH}}{n \times T}$$

Force times length has dimension of energy. It follows that R has the dimension of energy per degree per mole. Some of the more useful values of R are given in Table 3.3.

Example 3.4

How many moles of hydorgen (H_2) are present in a   500 cm^3 sample of hydrogen gas at a pressure of 760 mm of Hg and a temperature of 300 K?

*Since the volume of a given mass of a gas depends on both temperature and pressure it is necessary to state the values of T and P when the value of V is stated. The volume of a given sample of a gas is normally reported at 273.15K (0°C)   and 101 33 kPa (1 atm) pressure. These values are called, STANDARD TEMPERATURE AND PRESSURE (STP).

TABLE 3.3

Values of the Ideal Gas Constant R in Different Units

0.0821	litre-atm K^{-1} mol^{-1}	8.31×10^{7}	erg K^{-1} mol^{-1}
82.1	ml-atm K^{-1} mol^{-1}	8.31	Joule K^{-1} mol^{-1}
62.3	litre-mm K^{-1} mol^{-1}	1.987	cal K^{-1} mol^{-1}

Solution

In SI units, $R = 8.31$ kPa dm^3 mol^{-1} K^{-1}. It is necessary therefore to express the pressure and volume in kilopascals and dm^3 respectively.

$$P = 760 \text{ mm Hg} = 101.3 \text{ kPa}$$
$$V = 500 \text{ cm}^3 = 0.500 \text{ dm}^3$$
$$T = 300 \text{ K}$$
$$n = ?$$
$$\text{Since } n = \frac{PV}{RT}$$
$$= (101.3 \times 0.500)/(8.31 \times 300)$$
$$= 2.03 \times 10^{-2} \text{ mol}$$

The above example shows how to calculate the number of moles of a gas if pressure, volume, and temperature are known. If in addition, the mass of the gas is also known, the molar mass of the gas can be calculated.

Example 3.5

The mass of 500 cm^3 of hydrogen gas at a pressure of 760 mm Hg and at temperature of 300K was found to be 4.09×10^{-2}g. Calculate the molar mass of hydrogen.

Solution

We already know from Example 3.4 that $n = 2.30 \times 10^{-2}$ mol. Now molar mass (M) is given by

$M = m/n$ where m is the mass in grams

Therefore, $M = (4.09 \times 10^{-2})/2.03 \times 10^{-2} = 2.01$ g mol^{-1}

The molar mass of a volatile liquid can be determined as in Examples 3.4 and 3.5, if the mass of the vapour of the liquid (instead of the mass of gas) is known. It should be noted that a knowledge of molar mass of a compound and its empirical formula permits determination of the molecular formula (see Example 1.3).

It is a straightforward matter to determine the pressure of a confined gas if, volume, temperature, and number of moles are known.

Example 3.6

2.802 g of N_2 (molar mass $= 28.02$ g mol^{-1}) gas is kept in a 1.00 L flask at 0°C. Calculate the pressure exerted by the gas.

Solution

We illustrate here the choice of an alternative system of units by taking R $= 0.0821$ L atm $mol^{-1}K^{-1}$. We are given

$$V = 1.00 \text{ L}$$
$$T = 0^0C = 273 \text{ K}$$
$$n = \frac{2.802}{28.02} = 0.1000 \text{ mol}$$
$$P = ?$$

$$P = \frac{nRT}{V}$$
$$= \frac{0.1000 \times 0.0821 \times 273}{1.00} = 2.24 \text{ atm}$$

In Example 3.5, we have used the equation $PV = \frac{m}{M} RT$ instead of the equation $PV = nRT$, by utilising the relation $n = \frac{m}{M}$ which expresses the fact that the number of moles of a substance is equal to the mass m of the substance divided by the molar mass. Since density (ρ) is mass per unit volume, i.e.,

$$\rho = m/V$$

It is possible to rewrite $PV = \frac{m}{M} RT$

$$\text{as } P = \frac{\rho}{M} RT$$

$$\text{or } M = \frac{\rho RT}{P}$$

This means that we can determine the molar mass M of a gaseous substance from its density at a given pressure and temperature. In general, the above equation permits determination of any of the four variables M, ρ, T, P, if the other three are known.

Example 3 7

The density of a gas was found to be 3.43 gL^{-1} at 300K and 1 00 atm. Calculate the molar mass.

Solution

$$P = 1.00 \text{ atm}; T = 300K; \rho = 3.43 \text{ gL}^{-1}$$

$$M = \frac{3.43 \times 0.0821 \times 300}{1.00} = 84.5 \text{ g mol}^{-1}$$

Molar volume of a gas: In section 4 of Unit 1, we had stated Avogadro's Hypothesis as "Equal volume of all gases at the same temperature and pressure contain equal number of particles". It is easy to see that this statement is a direct consequence of the ideal gas law, $PV = nRT$, since if P, V, and T are the same, then n must be the same, i.e., the number of particles must be the same. It also follows that at the same temperature and pressure n moles of any gas occupy the same volume. In particular, the volume occupied by 1 mol of any gas known as the *molar volume* must be the same at the same temperature and pressure. The molar volume of an ideal gas at STP is 22.4 L. Since 1 mol contains 6.02×10^{23} particles, 22.4 L of an ideal gas contains these many particles at 273 K and 1 atm. By combining Avogadro's Hypothesis with the ideal gas law, it is possible to deduce volume relationships between reactants and products in a balanced chemical equation.

Example 3.8

Butane (C_4H_{10}) gas burns in oxygen to yield carbon dioxide and water. The chemical equation for the reaction is:

$$2C_4H_{10} + 13O_2 \longrightarrow 8 CO_2 + 10 H_2O$$
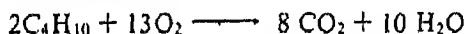
5.00L of butane is burned in excess oxygen at 27°C and 1 atm. Calculate how many litres of carbon dioxide are formed

(a) at 27°C and 1.0 atm.

(b) at 67°C and 2.0 atm.

Solution

In part (a), CO_2 is formed at the same temperature and pressure as butane (C_4H_{10}). It follows from the chemical equation that 2 litres of butane will yield 8 litres of CO_2. Hence, 20.0 litres of CO_2 will be released when 5.00 litres of butane are burned in oxygen.

In part (b), we have to calculate the amount of CO_2 at 67°C (340K) and 2 atm. Thus we need to calculate how the volume of CO_2 is going to change as we change the temperature and pressure from the initial condition (i.e., 300K, 1.0 atm) to the final condition (i.e., 340K, 2.0 atm).

$$P_1 = 1.0 \text{ atm}; T_1 = 300K; V_1 = 20.0 \text{ litres}$$

$$P_2 = 2.0 \text{ atm}; T_2 = 340 \text{ K}, V_2 = ?$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or $\quad V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{1.00 \times 20.0 \times 340}{2.0 \times 300} = 11.3 \text{ l.}$

In the next example, we show the application of the ideal gas law to a reaction in which only one of the constituents is a gas.

Example 3.9

A simple method of producing oxygen in the laboratory is by heating potassium chlorate ($KClO_3$) in the presence of manganese dioxide (MnO_2) which acts as a catalyst. Calculate the volume of oxygen at $0°C$ and 1 atm when 12.25 g of $KClO_3$ are heated in the presence of MnO_2.

Solution

The equation for the reaction is

$$2KClO_3 \longrightarrow 2KCl + 3 O_2$$

Which means that 3 mol of O_2 are produced by heating 2 mol of $KClO_3$. Now 12.25 g of $KClO_3$ are equal to 0.10 mol since the molar mass of $KClO_3$ is $(39 + 35.5 + 3 \times 16)$ g or 122.5 g.

It follows from the equation that 0.10 mol of $KClO_3$ will produce 0.15 mol of O_2.

The temperature and pressure for the reaction corresponds to standard condition, i.e., STP. We further know that for an ideal gas the molar volume is 22.4 l, i.e.,

Volume of 1 mol of O_2 at STP = 22.4 L

Volume of 0.15 mol of O_2 at STP = 22.4×0.15 L = 3.4 L.

3.1.6   Dalton's Law of Partial Pressure

So far we have considered the relation between P, V, T, and n for a gaseous system in which only one component is present. If several components are present in a gaseous mixture, it is necessary to make some modifications. The relationship between P, V, T, and n in the mixture of non-reacting gases is illustrated by the experiment shown in Fig. 3.7. The three vessels maintained at the same temperature have equal volume and each has a manometer for measuring the pressure of the gas. Let a sample of nitrogen at pressure P_1 be pumped into one vessel and a sample of oxygen at pressure P_2 into the second vessel. Now if both the samples are pumped into a third vessel, the pressure here is observed to be the sum of P_1 and P_2. This shows that each component independently contributes to the total pressure.

This behaviour of a mixture of two gases was first expressed in 1807 by John Dalton and is known as Dalton's law of partial pressure. This law states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the pressures which each component would exert if placed separately in the container.

$P_t = P_1 + P_2 + P_3 + \cdots\cdots$ (T, V are constant) where P_t is the total pressure and $P_1, P_2, P_3, \ldots\ldots$etc, are partial pressures of components 1, 2,3, $\ldots\ldots$etc.
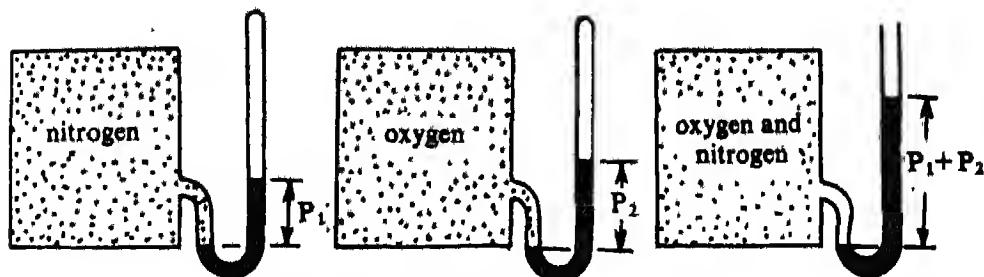
Fig. 3.7 *Dalton's law of partial pressures*

Example 3.10
A 5.00 L flask contains 19.5 g of sulphur trioxide (SO_3) and 1.00 g of helium (He). The temperature of the flask is 20°C. Calculate the partial pressures exerted by SO_3 and by He and the total pressure of the gaseous mixture.

Solution
We make use of Dalton's law of partial pressure according to which each gas in a mixture behaves as if it alone occupied the container. Thus, we will apply the ideal gas law to SO_3 and He separately to determine their partial pressures. To do this, we need to calculate the number of moles of each.

Molar mass of $SO_3 = (32.1 + 3 \times 16.0) = 80.1$ g

Molar mass of He $= 4.00$ g

Number of moles of $SO_3 = n_1 = \dfrac{19.5}{80.1} = 0.243$ mol

Number of moles of He $= n_2 = \dfrac{1.00}{4.00} = 0.250$ mol

Partial pressure of $SO_3 = P_1 = \dfrac{n_1 RT}{V} = \dfrac{0.243 \times 0.0821 \times 293}{5.00}$

$$= 1.17 \text{ atm}$$

Partial pressure of He $= P_2 = \dfrac{n_2 RT}{V} = \dfrac{0.250 \times 0.0821 \times 293}{5.00}$

$$= 1.20 \text{ atm}$$

The total pressure (P) is the sum of partial pressures i.e
$$P = P_1 + P_2 = 1.17 + 1.20 = 2.37 \text{ atm}$$

3.2   KINETIC MOLECULAR THEORY OF GASES

We have so far examined the behaviour of gases from an experimental point of view. Thus, Boyle's law, Charles' law, etc. are concise statements of experimental facts observed in the laboratory. Conducting careful experiments is an important aspect of the scientific method as it tells us *how* nature is behaving. However, once the experimental facts are established, a scientist is curious to know *why* nature is behaving in that way. For example, we would like to know "Why is the volume of a gas inversely proportional to pressure as stated by Boyle's law?" To answer such questions, it becomes necessary to construct a theory. A theory is a model (i.e., a mental picture) of nature which enables us to better understand our observations. The theory which provides an explanation of the observed features of gaseous behaviour is known as the *kinetic molecular theory*. It is an extension of the atomic molecular theory studied in Unit 1; it assumes that not only are all substances made of atoms and molecules but also that these atoms and molecules are in a constant state of motion

3 2.1   The Microscopic Model of a Gas

The kinetic molecular theory of gases makes the following assumptions. Since all the assumptions relate to atoms and molecules which cannot be seen, the kinetic theory is said to provide a *microscopic* model of a gas. However, calculations and predictions based on the kinetic theory agree very well with the experimental observations thereby establishing the correctness of this model.

(i)   A gas consists of a large number of particles (atoms or molecules) that are so small and so far apart (on the average) that the actual volume of the molecules is negligible compared to the empty space between them. This assumption easily explains the great compressibility of gases.

(ii)   There are no attractive forces between the particles so the particles move independently of each other. The support for this assumption comes from the observation that the gases expand to occupy all the space available to them

(iii)   The particles of a gas are not at rest but in a state of continuous motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not what is observed.

(iv)   The particles move randomly in straight lines. Collisions with each other and with the walls of the container cause a change in the direction of the movement. In these collisions, it is assumed that there is no net loss of kinetic energy although there may be a transfer of energy between the colliding particles. (Collisions in which total kinetic energy remains constant are called *elastic collisions.*) This assumption is made because if there were loss of kinetic energy, the motion of the particles would

eventually stop. This would lead to the 'collapse' of the gas, contrary to what is observed.

(v) The pressure exerted by a gas is the result of collisions of the particles with the walls of the container.

(vi) At any particular time, different particles in a gas have different speeds and hence different kinetic energies. This assumption is reasonable because a large number of particles imply a large number of collisions. As particles collide, we expect their speeds to change. Even if all the particles had the same initial speed, molecular collisions will disrupt this uniformity. Consequently, different particles must have different speeds which will be constantly changing. However, it is possible to show that even though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature. This distribution is referred to as the *Maxwell-Boltzmann distribution* in honour of the scientists who first discovered it. As we shall find out later, the Maxwell-Boltzmann distribution can be theoretically derived and it has also been verified experimentally. The distribution at two different temperatures is shown in Fig.3.8.
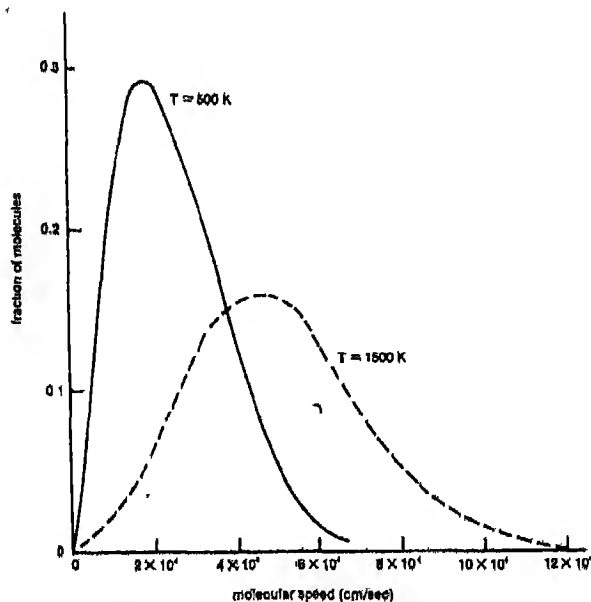
Fig. 3.8   *Molecular speed distribution at two temperatures.*

(vii) If a molecule has a variety of speeds, then it must nave a variety of kinetic energies. Under these circumstances, we can only talk about average kinetic energy It is assumed in the kinetic theory that the average kinetic energy of a molecule is directly proportional to the absolute temperature. This assumption is made because it alone leads to the equation PV=nRT, obeyed by gases at ordinary temperatures and pressures.

THE RELATION BETWEEN AVERAGE KINETIC ENERGY AND ABSOLUTE TEMPERATURE

You will learn in advanced courses that the mathematical treatment of the kinetic model of a gas yields the following equation.

$$PV = 1/3 \ Nmu^2$$

where N is the number of molecules in volume V, m is the mass of a molecule and u is the root mean square velocity of the molecules.
Since Nm = M, the molecular mass, we can write,

$$PV = 1/3 \ Mu^2$$

We also know that PV = RT for one mole.

$$\text{or} \quad RT = 1/3 \ Mu^2$$

$$u^2 = \frac{3RT}{M}$$

$$\text{Therefore, } u = \sqrt{\frac{3RT}{M}}$$

The root mean square velocity, u, can thus be calculated. For H_2 molecule, u is 1.84×10^5 cm/ sec or 1.84 km/sec. For N_2 molecule, u is 0.493 km/sec.

The equation, $\qquad RT = \frac{1}{3} Nmu^2$ can be written as,

$$RT = \frac{2}{3} \times \frac{1}{2} \times Nmu^2$$

Since $1/2 \ mu^2$ is equal to the average kinetic energy, E_k

$$RT = \frac{2}{3} E_k \qquad \text{or} \quad E_k = \frac{3}{2} RT$$

We thus see that the average kinetic energy is proportional to absolute temperature.

Explanation of Gas Laws on the Basis of the Kinetic Theory
The molecular model of gases satisfactorily explains the gas laws as shown below.

(i) *Boyle's Law:* The kinetic theory assumes that a gas exerts pressure because of the collisions of the particles with the walls of the container. The magnitude of pressure should therefore depend on the frequency of collisions, i.e., on how often the collisions take place. The frequency obviously depends on the number of particles and on their average speed. When the amount of gas and the temperature remain constant the number of molecules and the average kinetic enegy—and hence the average speed—remain constant. (The second part follows from the assumed proportionality between temperature and average kinetic energy, i.e , when temperature is constant so is the average kinetic energy.) Now, if the volume of a fixed amount of gas is reduced at constant temperature, then the particles will have less space in which to move about. Consequently, they will collide with the walls more frequently thus causing increased pressure in agreement with Boyle's law.

We shall leave it to you to reason out, on the basis of the molecular model, what should happen if the volume of a fixed amount of gas is increased at constant temperature. Does your prediction agree with Boyle's Law?

(ii) *Charles' Law:* When a fixed amount of gas is heated at constant volume, the molecules absorb energy and move faster. They therefore hit the walls harder often resulting in increase of pressure. However, if the heating is done keeping the pressure constant, then the volume has to increase. The latter compensates the increased force of collisions by decreasing the number of collisions per unit area.

(iii) *Dalton's Law:* In the absence of attractive forces, the particles of a gas behave independently of one another. This will be true even if there are more than one type of particles as happens in a mixture of gases

The partial pressure of a gas depends only on the number of its molecules striking the walls and it is unaffected by the pressure of the molecules of other gases. Since the total pressure exerted is due to the impact of particles of all the gases, it follows that the total pressure will be equal to the sum of the partial pressures.

A few comments on the Maxwell-Boltzmann distribution of molecular velocities (or speeds) shown in Fig.3.8 would be in order. According to this figure, there is only a small number of molecules with very low velocities or with very high velocities. Most molecules have intermediate velocities. The largest number of molecules have a velocity corresponding to the maximum of the curve. (This velocity is referred to as the *most probable velocity).* This behaviour is nothing unique to gas molecules alone. Such distributions are commonly found in other situations as well and many of them may be familiar to you. Let us consider one example.

In an examination taken by a large number of students (say 100 or more), if we look at the mark scored by students, we shall find an interesting pattern. Very few students get 100% marks and very few (or none) get 0% marks. Most students get marks between 0 and 100%. If we plot the number of students versus percentage marks we shall obtain a curve similar to the ones in Fig 3.8. The maximum number of students get a percentage (corresponding to the maximum in the curve) which represents the average performance of the class.

In Fig.3.8 we have shown velocity distribution curves at two temperatures. We see that the most probable value of the velocity (corresponding to the maximum in the curve) is higher at the higher temperature. This is what we would expect. As the temperature increases, the average velocity (average kinetic energy) of molecules should increase and more molecules should possess higher velocities.

We conclude this part with a couple of calculations which nicely substantiate the fact that a gas is mostly empty space.

Example 3 11

Atomic and molecular sizes are typically of the order of a few Angstroms ($1\overset{\circ}{A}$ = 10^{-10} m) Assuming that a N_2 molecule is spherical in shape with radius (r) = 2×10^{-10}m (200 pm or 2×10^{-8} cm), calculate:

    (i) the volume of a single N_2 molecule.

    (ii) the percentage of empty space in one mole of N_2 gas at STP.

Solution

    (i) Since the volume of a sphere is equal to $4/3$ (πR^3) where R is the radius, the volume of a N_2 molecule is:

$$\frac{4 \times 22}{3 \times 7} \times (200 \times 10^{-8})^3 \text{ cm}^3 = 3.35 \times 10^{-23} \text{ cm}^3 \text{ per molecule}$$

    (ii) To calculate the empty space, we first calculate the total volume of Avogadro's number of N_2 molecules. This volume is: 6.02×10^{23} molecules $\times 3.35 \times 10^{-23}$ cm^3 per molecule = 20.2 cm^3 per mole.

        However, the volume occupied by 1 mole of N_2 gas at STP is 22,400 cm^3 Hence the difference (i.e., 22,400 cm^3 − 20.2 cm^3 = 22,379.8 cm^3) is empty space

$$\therefore \text{ Percent empty space} = \frac{\text{Empty volume}}{\text{Available volume}} \times 100$$

$$= \frac{22,379.8}{22,400} \times 100 = 99.9\%$$

This calculation shows that particles of a gas occupy only a tiny fraction of the total gaseous volume. An overwhelming fraction of space in a gas is thus empty space.

Example 3.12

Calculate the average volume available to a molecule in a sample of nitrogen gas at STP (i.e., at 273K and 1 atm). What is the average distance between neighbouring molecules if a nitrogen molecule is assumed to be spherical?

Solution

One mole of nitrogen occupies 22.4L (22,400 cm^3) at 273K and 1 atm. Since a mole of nitrogen has 6.02×10^{23} molecules of N_2 it follows that the number of molecules per cm^3 is.

$(6.02 \times 10^{23})/22,400 = 2.69 \times 10^{19}$ molecules per cm^3.

The volume available per molecule is

$1/(2.69 \times 10^{19}) = 3.72 \times 10^{-20}$ cm^3 per molecule

To get the average distance between neighbouring molecules, we note that the volume of a spherical object is $4/3 (\pi R^3)$, where R is the radius. Since the volume available per molecule is found to be 3.72×10^{20}cm^3, we have

$$\frac{4}{3}(\pi R^3) = 3.72 \times 10^{-20} \text{ cm}^3$$

$$\text{or} \quad R^3 = \frac{3.72 \times 10^{-20} \times 3 \times 7 \text{ cm}^3}{4 \times 22}$$

$$= 8.88 \times 10^{-21} \text{ cm}^3$$

Hence $\quad R = 20.7 \times 10^{-8}$ cm

This means that the volume available (on an average) to a N_2 molecule is the volume of a sphere whose radius (R) is 20.7×10^{-8} cm. It follows that the average distance between two neighbouring molecules will be $2R = 41.4 \times 10^{-8}$ cm. In the previous example, the radius of a N_2 molecule is given as 2×10^{-8} cm, i.e., the diameter is 4×10^{-8} cm. Our calculation shows that the average distance is nearly ten times the molecular size which confirms the fact that much of the space in a gas is empty space.

A similar calculation for liquid nitrogen and solid nitrogen shows that the average distance in the liquid state and the solid state is of the same order as the molecular diameter implying thereby that the molecules touch each other. This explains why it is difficult to compress liquids and solids but easy to compress gases.

3.2.2 Deviation from Ideal Behaviour

The PVT behaviour of gases has so far been based on the ideal gas equation, $PV = nRT$. This simple equation of state is approximately obeyed by all gases. Deviations are however observed if measurements are carried out at high pressures or low temperatures. A convenient way of showing the deviation of real gases from ideal

behaviour is to write the ideal gas equation in the form,

$$PV = ZnRT \text{ where Z is unity.}$$

Or, $Z = PV/nRT = 1$ for an ideal gas

The quantity $Z = PV/nRT$ is called the compressibility factor; $Z = 1$ under all conditions for an ideal gas and the departure of a real gas from ideality is then measured by the deviation of the compressibility factor from unity. The extent of deviation from ideality depends upon the temperature and pressure.

The quantity Z often exhibits both positive (when $Z>1$) and negative (when $Z<1$) deviation from unity Fig. 3.9 shows some examples of the non-ideal behaviour of real gases. We see that even at 1 atm pressure there are small deviations from ideality for all gases at any temperature. The extent of deviation at any given temperature and pressure, depends on the nature of the gas. Z approaches unity as
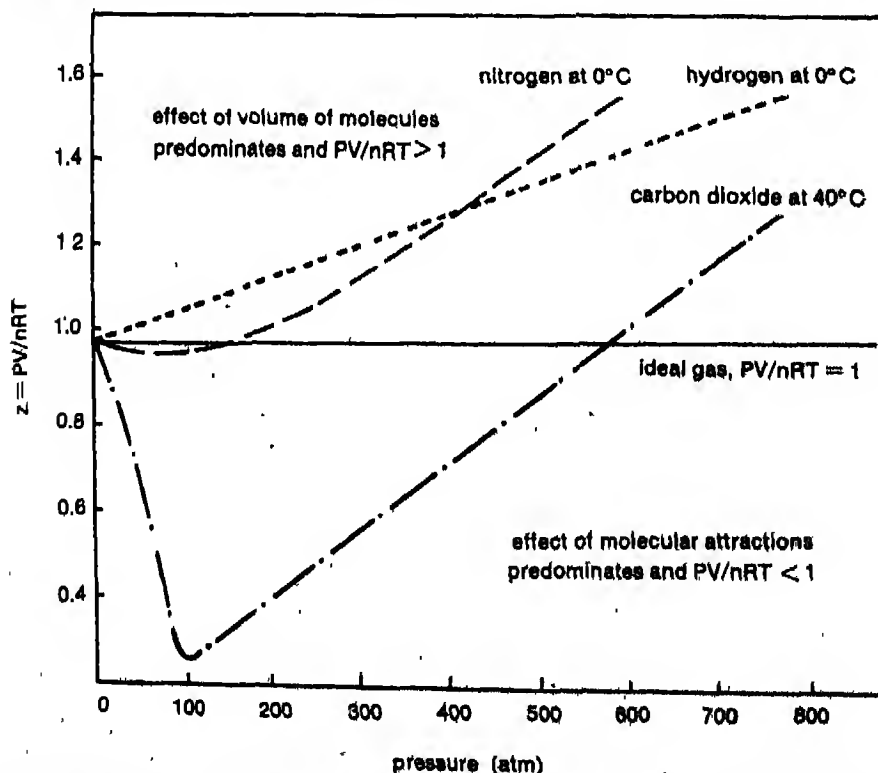
Fig. 3.9 Deviations from ideal gas behaviour, shown by a plot of the compressibility factor Z = PV/nRT as a function of P for some gases.

pressure approaches zero which means that $PV = nRT$ is an approximate equation applicable at low pressure.

Why do gases deviate from ideality? While discussing the ideal gas equation, we had made a number of assumptions. The fact that this equation is not obeyed means that some of the assumptions may not be valid. Let us re-examine two of the assumptions: (i) that the volume of the molecules is negligible compared to the empty space between them, and (ii) that there are no attractive forces between the molecules.

We know that the volume of a gas can be reduced by applying pressure or by cooling the gas until the gas condenses into a liquid or solid (with finite volume). This implies that molecules in the gas must also occupy some volume. Under normal conditions of temperature and pressure, the volume of molecules is just about 0.1 per cent of the total volume of the gas. At very high pressures (say 100 atm) or at very low temperatures, the total volume of the gas decreases appreciably (while the actual volume of the molecules remains the same). Under these conditions the volume of the molecules can no longer be neglected.

The assumption that there are no intermolecular forces between gas molecules is not strictly true. The very fact that gases can be condensed to liquids and solids indicates that there are attractive forces present between molecules. The attractive forces become large when molecules are crowded together. The pressure of a gas arises from the transfer of momentum between the colliding molecules and the walls of the container. If there are attractive forces between molecules, the transfer of momentum is somewhat impeded by the interaction between molecules. Consequently, the actual pressure will be less than the pressure predicted by the ideal gas equation.

In Fig. 3.9, the regions where these two effects predominate are shown. For hydrogen at $0°C$, the molecular attractive forces are weak and the size effect dominates its behaviour. For nitrogen at $0°C$, the attractive forces are large enough to cause negative deviation up to about 150 atm, beyond which the size effect dominates. For CO_2, intermolecular attraction is large even at $40°C$. The two effects compensate each other at 150 atm and 600 atm respectively in N_2 and CO_2 and $PV/nRT = 1$. At very low pressures gas molecules are widely separated and both these effects become negligible. Accordingly, as the pressure is decreased, the behaviour of gases approximate more and more closely that of the ideal gas. At high temperatures, molecules possess greater kinetic energy and their tendency to aggregate decreases and the behaviour of gases is close to the ideal gas behaviour. Thus, we see that under the normal conditions in the laboratory, deviation from ideality is not very significant.

A modification of the ideal gas equation was proposed by van der Waals in 1873 by taking into account both the factors mentioned above. The modified equation for one mole of a gas is given by

$$(P + \frac{a}{V^2})\ (V - b) = RT$$

where a and b are constants depending on the nature of the gas. The term a/V^2 corrects the deviation in pressure while the term b corrects the volume.

3.3 THE SOLID STATE

In this section, we will study the nature of the solid state. In crystalline solids (or crystals), there is a regular order in the arrangement of the atoms, ions or molecules constituting the solid and these particles are held together by fairly strong forces. We are familiar with many of the properties of solids on the basis of our daily experiences

(i) Solids are rigid and have definite shape.

(ii) Solids maintain their volume independent of the size or shape of the container in which they are placed.

(iii) Solids are nearly incompressible.

(iv) Solids diffuse very slowly compared to liquids or gases.

The above properties suggest that particles constituting solids occupy fixed positions.

A study of solids is mainly a study of crystals since a large number of solids are crystalline. Many naturally occurring solid substances occur in the form of crystals. You must have seen crystals of common salt (sodium chloride), crystals of ice and blue crystals of copper sulphate. Crystals are characterised by the regular arrangement of atoms, ions or molecules in all the three dimensions. This regular arrangement gives rise to *long range order* in crystals. In a crystal of sodium chloride, experiments show that Na^+ and Cl ions are located at alternate sites as shown below:

$$Na^+ \quad Cl^- \quad Na^+ \quad Cl^- \quad Na^+ \quad Cl^-$$
$$Cl^- \quad Na^+ \quad Cl^- \quad Na^+ \quad Cl^- \quad Na^+$$
$$Na^+ \quad Cl \quad Na^+ \quad Cl^- \quad Na^+ \quad Cl^-$$
$$Cl^- \quad Na^+ \quad Cl^- \quad Na^+ \quad Cl^- \quad Na^+$$
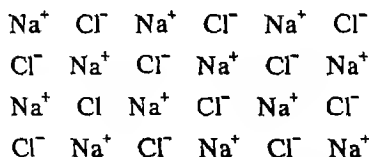
The arrangement shown above is only in two dimensions. In three dimensions we find that each Na^+ ion is surrounded by a fixed number (six) of Cl ions and vice versa The origin of the three dimensional order in NaCl crystals is due to the strong coulombic attraction between Na^+ and Cl^- ions. A similar regular arrangement is also found in other solids. The constituent particles in crystals are generally held by strong interatomic, interionic or intermolecular forces. Particles in a solid do not possess translational motion, but they vibrate about their equilibrium positions.

Let us now consider what happens when a crystal is heated. As heat is supplied to the crystal the constituent particles vibrate more vigorously about their equili-

brium positions. Eventually the kinetic energy of the particles becomes sufficiently large to overcome the binding forces and the solid melts to form a liquid. The temperature at which a solid melts at normal pressure is called the melting point of the solid. Melting points of some common substances are given in Table 3.5.

TABLE 3 5

Melting Points of a Few Substances

Solid	Melting point (K)	Solid	Melting point (K)
Oxygen	55	Sodium	371
Nitrogen	63	Sodium chloride	1077
Ethyl alcohol	159	Magnesium chloride	1260
Carbon tetrachloride	249		

Melting points of solids give a rough idea about the nature of the binding forces between the molecules, ions or atoms constituting the solid. Ionic solids (e.g., sodium chloride, magnesium chloride) possess high melting points because of strong (coulombic) attractive forces. On the other hand, solids having weak attractive forces show low melting points (e.g , oxygen, nitrogen). We will study in Unit 6 about different types of bonding in solids.

There are many solids where there is no long range order in the arrangement of the constituent particles. Such solids are called amorphous solids. Glass is an example of an amorphous solid. Although there would be no long range order in amorphous solids, there would be some order in the arrangement of the nearby neighbours (e.g., in ionic materials, the oppositely charged ions would still surround an ion). Such order lasting only short distances (unlike the infinite range of long range order) is called short range order. We thus see that crystals have both short range and long range order, while amorphous solids have only the former.

Unlike crystalline solids, amorphous solids do not exhibit sharp melting points

3.3.1 Classification of Solids

Different structural features of solids can form the basis for classifying them. They may be roughly divided into two classes: TRUE SOLIDS AND PSEUDO SOLIDS. A distinctive feature of solids is that they are rigid. A true solid has a shape which it holds against mild distorting forces. A pseudo solid lacks this character. It can be more easily distorted by bending and compressing forces. It may tend to flow slowly even under its own weight and lose shape Pitch and glass are two examples of pseudo solids. In old buildings, window glasses are found to have become somewhat

thicker at the bottom and thinner near the top. The rigidity and shape of pseudo solids are only apparent. Such substances are better described as SUPERCOOLED LIQUIDS. We shall not pursue their study at present except to say one thing: pseudo solids do not melt sharply on being heated: they gradually soften over a wide range of temperatures and eventually lapse into a liquid state.

Solids may exist in shapeless AMORPHOUS forms or in well shaped CRYSTALLINE forms. Crystalline solids may be further classified according to the nature of particles constituting them and the binding forces between them (Table 3.6)

Amorphous solids include substances like glass, fused silica, rubber and polymers of high molecular masses. They may even have small parts in crystalline and the rest in non-crystalline form. Crystalline parts of an otherwise amorphous substance are called CRYSTALLITES. When we try to cut a crystalline solid with a sharp edged tool it gives a clean cleavage, but an amorphous substance gives an irregular or conchoidal fracture (Fig. 3.10) Crystalline substances have a definite rigid shape or morphology. Every crystal is contained within a well defined set of surfaces which are called PLANES. Such a substance also has: (i) a sharp melting point, (ii) a characteristic heat of fusion, (iii) a definite three dimensional arrangement of constituent particles, and (iv) general incompressibility.

TABLE 3 6

Crystal Types According to Constituent Particles

Crystal type	Constituent particles	Major binding forces	Properties	Examples
Molecular	Small molecules	van der Waals forces	Soft, low melting, volatile, electrical insulators, poor thermal conductors, low heats of fusion	Solid CO_2 and CH_4 Wax, iodine, ice, sulphur
Ionic	Network of positive and negative ions systematically arranged	Strong electrostatic attractions	Brittle, high m.p., poor conductors of electricity and heat, very high heats of fusion	Salts like NaCl, LiF, $BaSO_4$
Covalent	A network of chemically bound atoms of one or more kinds	Covalent bond forces	Very hard, high m.p., poor conductors of heat and electricity, high heats of fusion	Diamond, silicon, quartz
Metallic	Positive ions in a sea of electrons	Electrical attraction	Very soft to very hard, low to high m.p., good conductors of electricity and heat, metallic lustre, ductile and malleable, moderate heats of fusion	Common metals and some alloys
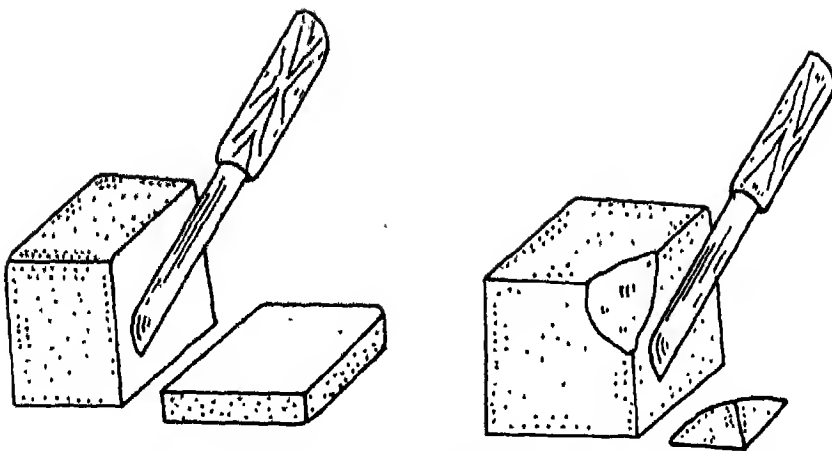
Fig. 3.10 *Cutting solids:* (a) *a crystal line solid gives a clean cut,* (b) *an amorphous solid gives an irregular cut*

3.3.2 X-ray Studies of Crystals

Much of our information about the structures of crystals at the level of molecules, atoms and ions has been revealed by their interactions with X-rays. Crystals are found to act as diffraction gratings for X-rays. This indicates that the constituent particles in crystals are arranged in planes at close distances in repeating patterns. W.L. Bragg and his father W.H. Bragg tried to locate relative positions of Zn and S atoms in a ZnS crystal by a detailed analysis of diffraction patterns formed with X-rays. Later, a method was developed by Debye, Scherrer and Hull in which the X-ray pattern could be obtained for a substance in powdered form instead of a single crystal. The diffraction pattern was taken on a circular film surrounding the powder target. Fig 3.11 shows one such diffraction picture.

To decide about distances between constituent particles in a crystal from the pattern shown in Fig. 3.11 is a problem in physics, and we shall not go into its details in the present course. We shall refer here only to the involved basic law known as Bragg's law. This is given by the following equation:

$$n\lambda = 2\,d\,\sin\theta$$
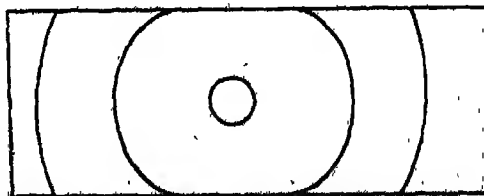
Fig. 3.11 *Diffraction pattern yielded by Debye-Scherrer-Hull Powder technique*
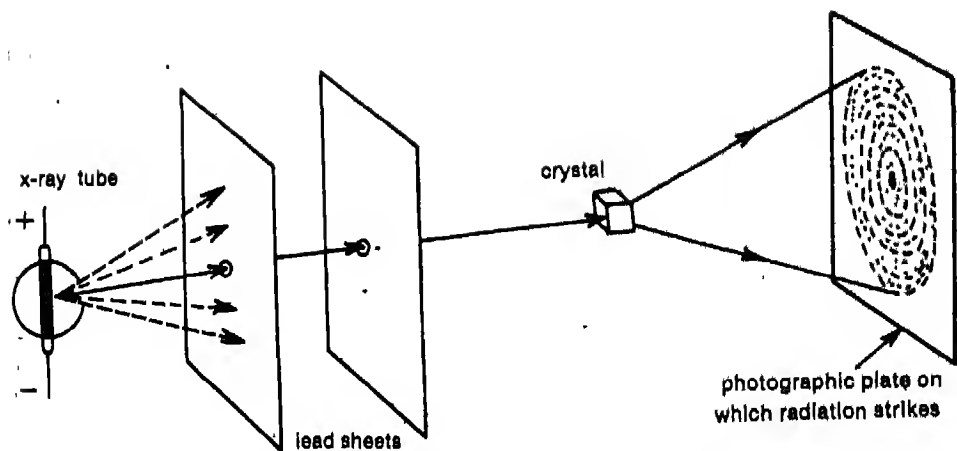
Fig. 3.12 *A simple set-up for X-ray diffraction*

CIRCULAR PHOTOGRAPHIC
FILM
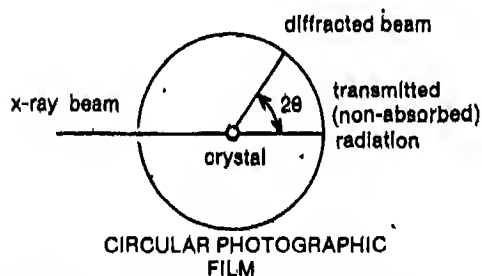
Fig. 3.13 *Simplified representation of X-ray diffrac-tion (in real situation many spots appear).*

Here d is the distance between planes of the constituent particles in the crystal, parallel to the plane on which the X-rays are incident, 2θ is the angle made by a diffracted X-ray beam with the direction of the incident beam, λ is the wavelength of X-ryas used, and n is an integer (1,2,3 .. etc.) which stands for the serial order of diffracted beams. Using Bragg's law we can calculate distances between repeating planes of particles in crystals or using crystals with known interplanar distances we can calculate the wavelengths of the X-rays used.

Example 3 13
What will be the wavelength of the X-rays which give a diffraction angle, 2θ equal to 16.80° for a crystal, if the interplanar distance in the crystal is 0.200 nm and only first order diffraction is observed?

Solution
In the equation, $n\lambda = 2 d \sin \theta$, n is equal to 1. Therefore,
$\lambda = 2 \times 0.2 \times 10^{-9} m \times \sin 8.40 = 0.4 \times 0.146 \times 10^{-9} m = 0.0584 \times 10^{-9} m$

3.3.3 Crystal Lattices and Unit Cells

The three dimensional distribution of constituent particles in a crystal can be found on the basis of diffraction of X-rays from the different faces of a crystal. Fig. 3.14 is an example of a three dimensional diagrammatic representation of a crystal. However, in the crystal, the constituent particles are packed as closely as possible. A representation of a crystal like Fig. 3.14, in which the locations of constituent particles are shown by points, is called the SPACE LATTICE or CRYSTAL LATTICE of

the crystal. For every crystal lattice it is possible to select a group of lattice points which sets the pattern for the whole lattice. This three dimensional group of points is called the UNIT CELL of the crystal and it is characterized by the distances, a, b and c along the three edges of the unit cell and the angles α, β and γ between the pairs of edges (b,c), (c,a) and (a,b) respectively. The whole crystal can be developed by a stepwise shifting of the unit cell in all the three directions. It is like building a whole block with the help of bricks.
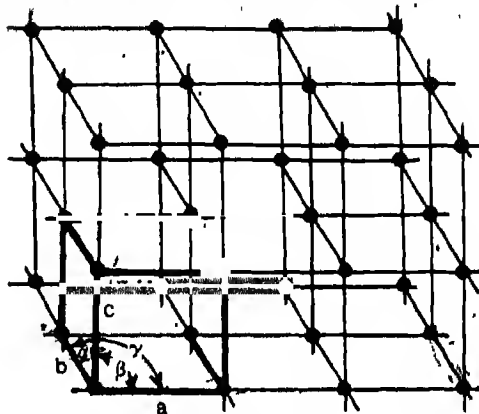
Fig. 3.14 *A simple depiction of crystal lattice and unit cell (the whole crystal is like a brickwork, heavy lines show unit cell).*

In all, seven types of BASIC OR PRIMITIVE UNIT CELLS have been recognised among crystals. They are called SEVEN CRYSTAL SYSTEMS or CRYSTAL HABITS. These are shown in Fig. 3.15 and their characteristics are listed in Table 3.7. In fact, a crystal consists of a large number of unit cells; this number depends on the size of the crystal. If the unit cell in a crystal lattice has lattice points only at the corners, the crystal is said to have a SIMPLE LATTICE. There are seven simple lattices based on the seven primitive unit cells. But all crystals do not have simple lattices. Some are more complex and it is not possible to discuss all of these at this stage. However, if we consider the cubic system of crystals, besides the simple cubic crystals, we often meet two other types of CUBIC CRYSTALS or CUBIC LATTICES. These are called FACE CENTRED CUBIC (fcc) and BODY CENTRED CUBIC (bcc) crystals. Unit cells of all the three cubic types of crystals are shown in Fig. 3.16.

During crystallisation all faces of a crystal do not grow at the same rate and, therefore, all crystals of a substance may not have the same ratio of axial edges as for the unit cell, but they will have the same axial angles. Actual crystals can differ in their final shapes and yet they may have unit cells of the same type.
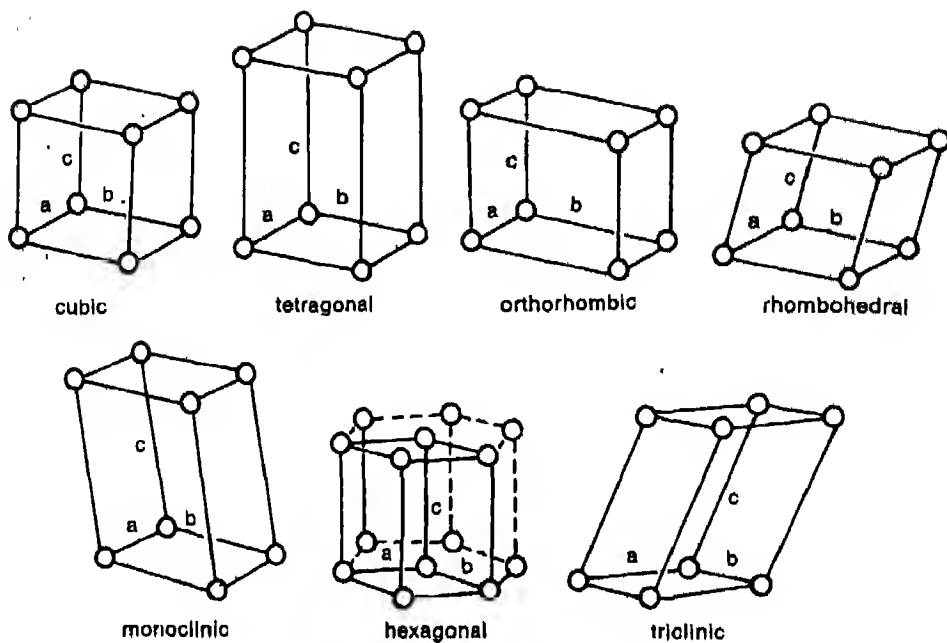
Fig. 3.15   *The seven primitive unit cells in crystals*
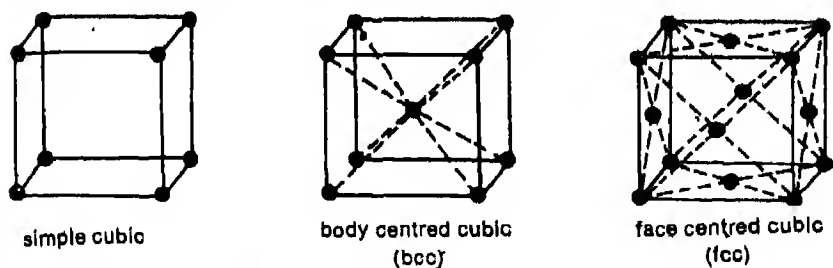
Fig. 3.16   *Three types of unit cells for cubic crystals*

TABLE 3.7 **Different Crystal Systems**

System	Axial distances	Axial angles	Examples
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	Copper, Zinc blende, KCl
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	White tin, SnO_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	Rhombic sulphur
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°$, $\beta\neq90°$	Monoclinic sulphur
Hexagonal	$a=b\neq c$	$\alpha=\beta=90°$; $\gamma=120°$	Graphite
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq90°$	Calcite
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq90°$	Potassium dichromate

3.3.4 Packing of Constituent Particles in Crystals

In the formation of crystals, the constituent particles get closely packed together. The available space is used most economically and a state of maximum possible density is reached. Since the constituent particles can be of various shapes, the mode of closest packing of particles will vary according to their shapes. We shall discuss here the packing modes of simple spherical particles to which the common constituent particles of crystals approximate. We shall further limit ourselves to spheres of equal size. By placing such spheres in a row in horizontal alignment, we develop an edge of a crystal [Fig. 3.17(a)]. By combining the rows we can build a crystal plane [Fig. 3.17(b)].

Combining of rows can be done in two ways with respect to the first row:

(i) The particles in the adjacent rows may show a horizontal as well as a vertical alignment and form squares. This type of packing is called a SQUARE CLOSE PACKING.

Fig. 3.17 *Packing of spheres for efficient use of available space.* (a) *edge formation,* (b) *two modes of plane formation*

(ii) The particles in every second row are seated in the depressions between the particles of the first row. The particles in the third row will be vertically aligned with those in the first row, and so on. This arrangement gives hexagonal patterns and is called HEXAGONAL CLOSE PACKING.

The second mode of packing is evidently a more efficient one. It leaves less space unoccupied by spheres. In square close packing, a central sphere is in contact with four other spheres and in the hexagonal close packing, a central sphere is in contact with six other spheres (Fig. 3.17).

For two dimensional packing, a hexagonally close packed layer gives a more efficient packing. Based on this, let us proceed further to consider a three dimensional packing maintaining a hexagonal close packed pattern for the layers Fig. 3.18 (a) shows the base layer in a crystal.

Fig. 3.18 *Layers in close packing of spheres:* (a) *Hexagonal close* packed base layer, (b) *two layers together*

In this layer, let the spheres be marked with the letter A and the two types of voids left between the spheres be marked with the letters B and C as shown in Fig.3 18 (a) If a second layer is placed with spheres vertically aligned with those in the first layer its voids will also cover the voids in the first layer. This will amount to an inefficient filling of space. If we arrange the second layer so that its spheres are seated in the B voids of the first layer, the C voids will remain unoccupied as no sphere can be seated in them under this plan (Fig. 3.18 (b)). In the second layer thus placed, we shall have some second layer voids over the C voids of the first layer. We shall call these voids (made of two voids in two different layers) as C voids. There will also be ordinary voids in the second layer over the positions of spheres in the first layer We can call these as B' voids of the second layer. While the B and C voids of the first layer are both triangular in shape, in the second layer, only the B' voids are triangular. The C' voids of the second layer are combinations of two triangular voids of the first and second layers with one triangle vertex upwards and the other triangle vertex downwards. A simple triangular void in a crystal gets surrounded by 4 spheres and is called a TETRAHEDRAL void or a hole. A double triangular void like C' gets surrounded by 6 spheres and is called an OCTAHEDRAL void (Fig.3.19)

If a third layer is placed over the second layer, so that the spheres cover the tetrahedral or B' voids, we get one type of three dimensional closest packing in which the spheres in every third or alternate layers are vertically aligned. This pattern is called the AB AB....pattern. Alternatively if the third layer sphere covers the octahedral or C' voids, we get a packing in which the spheres in every fourth layer will be vertically aligned. This gives the ABC ABC.... type pattern of stacking spheres. Both stacking methods are equally efficient though different in form. They can be repeated to any length. In a three dimensional packing of spheres the AB AB....packing is called the HEXAGONAL CLOSE PACKING (hcp) and the ABC ABC.... packing is called the CUBIC CLOSE PACKING (ccp). The ccp type packing tallies with
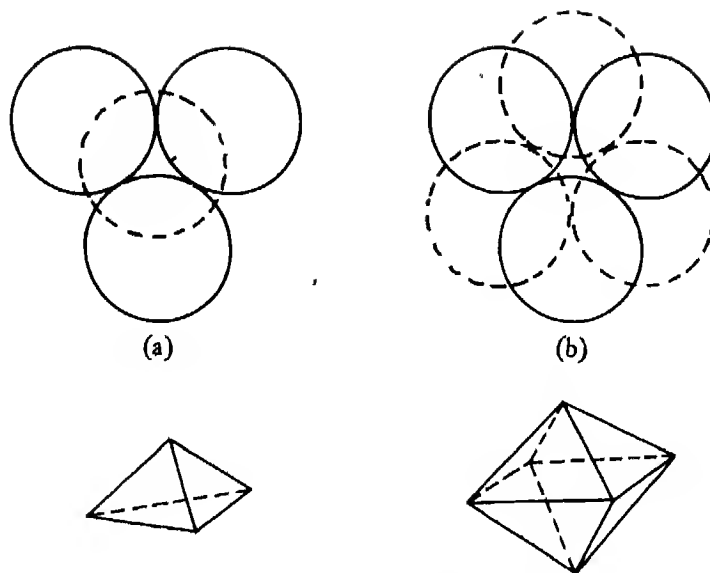
Fig. 3.19 *Two types of voids in crystals* (a) *tetrahedral void*, (b) *octahedral void*

the fcc type packing described earlier. Molybdenum, magnesium and beryllium crystallise in the hcp structure. Iron, nickel, copper, silver, gold and aluminium crystallise in the ccp structure.

The voids or holes in crystals are also called INTERSTICES. Their sizes acquire importance when some non-lattice atoms (such as H, B, C, N) or ions are to be accommodated in them. When transition metals form crystals of hydrides, borides, carbides, and nitrides, the respective non-metals are accommodated in the interstices. *Coordination Number.* In the hcp and ccp modes of stacking, a sphere will be in direct contact with 6 other spheres in its own layer. It will also be directly touching 3 spheres in the layer above and 3 in the layer below. Thus, a sphere has 12 closest neighbours in hcp and ccp stacks. It is said to have a *coordination number* of 12. In any crystal lattice, the number of closest neighbours of any constituent particle is called its COORDINATION NUMBER. Coordination numbers of 4, 6, 8 and 12 are quite common in various types of crystals.

3.4 THE LIQUID STATE

We have discussed the nature of the gaseous state in sections 3.1 and 3.2, and the nature of the solid state in section 3.3. We now take up the study of the third state of matter namely the liquid state. The fact that the volume of particles (i.e., atoms or molecules) of a gas is negligible compared to the volume occupied by the gas and

the fact that the forces between the particles are also negligible, makes the behaviour of gases rather easy to understand Both these features are   absent in the liquid state, the molecules of a liquid are close together and the attractive forces between them are strong. Compared to solids, molecules in liquids do not occupy fixed positions showing regular patterns. Thus liquids are neither completely disordered (as gases are) nor completely ordered (as solids are). This intermediate situation characterised by partial order and partial disorder complicates the study of liquids. In terms of the kinetic theory model, the nature of the liquid state is described as follows (i) There are appreciable attractive forces between the molecules. (ii) The molecules are relatively close together (iii) The molecules are in constant, random motion (iv) The average kinetic energy of molecules in a given sample is pro-portional to the absolute temperature .

LIQUID CRYSTALS

In a temperature range just above the melting point, some substances are able to exist in a definite pattern as in a solid but can flow as in a liquid. The molecules of such substances have unusual shapes; they may be long and cylindrical (rod-like) or large and flat (plate-like). These types of molecules are arranged in layers such that they move within a layer but not between the layers. Since the layers are static, a crystalline structure is possible which can diffract light. A liquid crystal reflects only one colour when white light falls on it because light of only one definite wavelength can satisfy the Bragg relationship $2d \sin \theta = n\lambda$. As temperature increases the kinetic energy of the molecules, the layers shift on heating and the reflected light correspondingly changes. Even small temperature changes can be detected easily by this method. Liquid crystals for example, can be used to locate veins since the temperature of a vein is slightly lower than that of the skin.

In the presence of even a weak electric field, rearrangement of the structure of the liquid crystal occurs changing it from a transparent to an opaque object. This property is used in the number displays of digital watches The requirement of very low fields makes this method consume little power and it is therefore widely used.

3.4.1 **Properties of Liquids**

Let us see how some of the observed macroscopic properties of the liquids can be understood on the basis of this model.

Volume: Liquids, unlike gases, have a definite volume They maintain their volume whatever be the shape or size of the container A 25 cm^3 sample of a liquid occupies 25 cm^3 whether it is placed in a beaker, a conical flask, or a large round-bottomed flask. A liquid remains confined to the lower part of the vessel whereas a gas spreads out to fill the whole volume available to it. In liquids the molecules are close together so that the mutual attractions are strong and hence they are not quite free to occupy any space. Gases do not maintain their volume because the molecules in a gas are relatively independent of one another and can move rather freely into any available space.

Density· The closer approach of molecules in the liquid state, also provides an explanation for the fact that densities of liquids are about thousand times greater than the densities of gases under comparable conditions Compare, for example, the density of water at $100^{\circ}C$ and 1 atm (0.958 g/cm^1) with that of water vapour at the same temperature and pressure (0.000588 g/cm^3).

Compressibility: Liquids are much less compressible than gases This is due to the fact that very little free space is available in liquids At $25^{\circ}C$, an increase in pressure from 1 atm to 2 atm, decreases the volume of a sample of liquid water by only 0.0045 per cent. The same change in pressure decreases the volume of an ideal gas by 50 per cent.

Diffusion· Like gases, liquids also diffuse but they do so rather slowly Diffusion involves movement of molecules from one position to another In the liquid state molecules undergo a number of collisions with the neighbouring molecules. In gases, there is less obstruction to the moving molecules because of the large empty space available for movement. The slower diffusion of a liquid is thus easily understandable.

When a few drops of ink are carefully released in water, there is a sharp boundary between the ink cloud and water. After some time the colour spreads throughout the water. The time taken for this to happen is appreciable. But when a drop of bromine is placed at the bottom of a container it becomes vapour which soon spreads throughout the container. In the gaseous state, the diffusion is very rapid.

Evaporation We know that when a liquid is placed in an open vessel it gradually disappears because the liquid is converted into its vapour. This process is known as evaporation. How does evaporation occur? Molecules in the liquid phase escape

from the surface of the liquid into the space above the liquid. This happens in spite of the strong attractive forces between the molecules in a liquid. To understand how molecules are able to escape from a liquid, remember that the molecules in a liquid are in constant motion and possess kinetic energy Although the temperature of the liquid is uniform and the average kinetic energy of the molecules is constant, not all the molecules have the same kinetic energy. In liquids, as in gases, molecules have a distribution of kinetic energies ranging from very low values to very high values. Consequently, a certain fraction of the molecules at the surface will have kinetic energies large enough to overcome the attractive forces of the neighbouring molecules and to escape into the space above the liquid surface. If the temperature is kept constant, the remaining liquid will have the same distribution of molecular energies and the most energetic fraction will continue to escape from the liquid into the vapour state. If the liquid is in an open vessel, evaporation will continue until no liquid remains.

The number of molecules escaping from the surface depends upon the intermolecular attractive forces When these forces are stronger fewer molecules escape. The ability to evaporate, or the volatility of a liquid, indicates the strength of intermolecular forces in the liquid. Ether evaporates more readily than alcohol and alcohol evaporates quicker than water. The intermolecular attractive forces vary in the order, ether < alcohol < water. A rise in temperature increases the kinetic

EVAPORATION AND COOLING

Since evaporation is a surface phenomenon, the increase in surface area increases the rate of evaporation. For example, a 5 cm^3 sample of ether placed in a beaker evaporates faster than the 5 cm^3 sample of ether placed in a test tube. That is why wet clothes are spread out for drying. A large surface area affords greater opportunity for the molecules of a liquid to escape. We have learnt that during evaporation, molecules having higher energy escape from the surface. They carry with them more than the average amount of kinetic energy and the less energetic molecules remain behind. This explains the common experience that temperature (which is proportional to kinetic energy) falls when liquids evaporate. For example, a drop of ether or chloroform produces a cool sensation on the skin due to evaporation. Can you now guess why a desert cooler is so effective in bringing down the temperature on a hot, dry summer day?

energy of molecules and they can escape more readily from the liquid surface. Hence evaporation of liquids increases with rise in temperature.

Heat of Vapourisation: The quantity of heat required to evaporate a given liquid at constant temperature is defined as the heat of evaporation or heat of vapourisation. The quantity of heat depends on the strength of forces of attraction between the molecules in a liquid . Water has a relatively high heat of vapourisation because of the presence of strong attractive forces When one mole of water is completely vapourised at 25°C, it absorbs 44,180 joule of energy from its surrounding

$$H_2O \ (l) + 44,180 \ joule \longrightarrow H_2O \ (g)$$
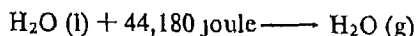
The molar heat of vapourisation of water at 25°C is thus 44.180 kJ.

Vapour Pressure: It was mentioned earlier that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed system such as a stoppered bottle, evaporation starts and after some time, the level of the liquid does not change further and remains constant. This may be explained as follows. Molecules which evaporate from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air. In the process they are pushed back to the surface of the liquid, a process referred to as condensation At the start, the rate of evaporation is much greater than the rate of condensation. But as molecules accumulate in the space above the liquid, the rate of condensation increases. Eventually, a condition is reached when the rate of condensation becomes equal to the rate of evaporation. When two opposing processes proceed at exactly the same rate, the system is said to be in a state of dynamic equilibrium (Fig 3.20). In such a state, there is no observable change in the
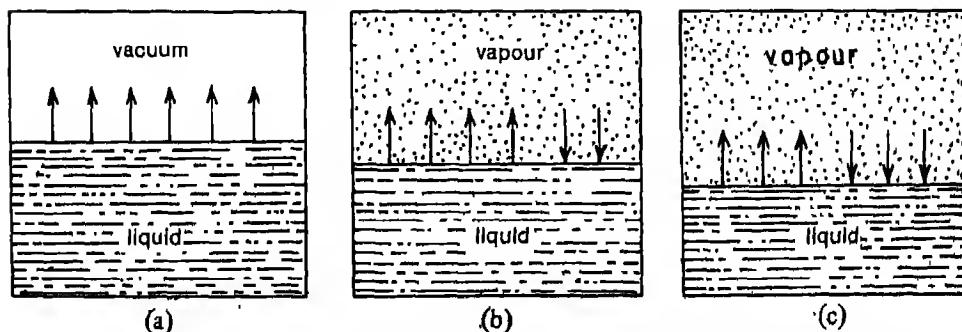
Fig. 3.20   *Attainment of equilibrium in the evaporation of liquid . (a) initial state, with evacuated space above liquid, (b) intermediate state, and (c) equilibrium state*

system. The amount of the liquid in the bottle remains constant. The number of molecules in the vapour above the liquid is also constant (since on an average, for every molecule that evaportes there is another which condenses). The molecules in the vapour phase exert pressure. This pressure is known as *equilibrium vapour pressure* or simply *vapour pressure*. The vapour pressure of a liquid has a characteristic value at a given temperature. The number of molecules escaping from the surface of the liquid increases with temperature resulting in an increase in the vapour pressure Fig 3.21 shows the temperature dependence of vapour pressure of some liquids.
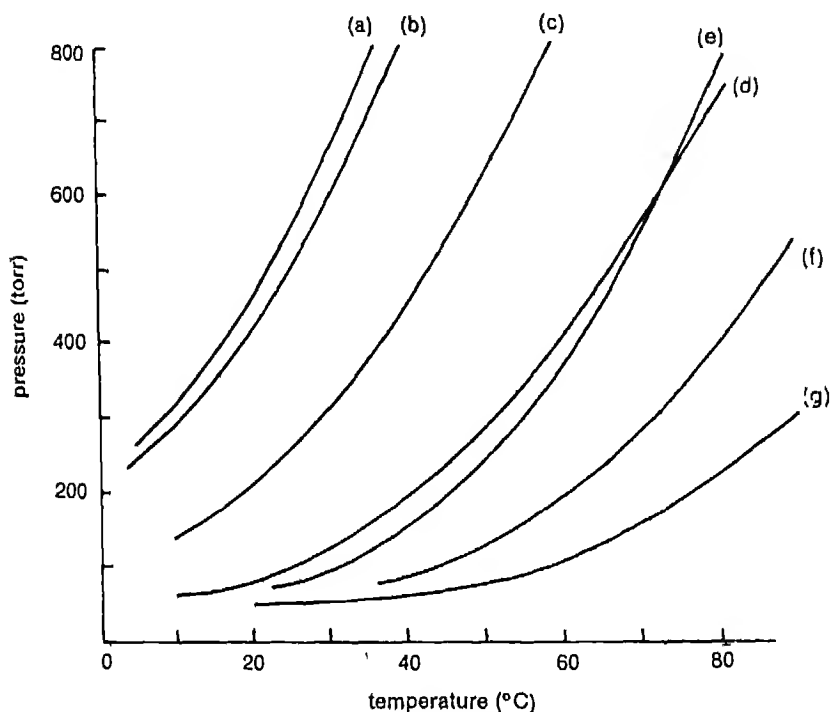
Fig. 3.21   *Temperature dependence of vapour pressure of liquids*   (a) *diethyl ether*, (b) *ethyl bromide*, (c) *acetone*, (d) *benzene*, (e) *ethyl alcohol*, (f) *water*, and (g) *octane*

Boiling: When a liquid is gradually heated, the temperature of the liquid rises and its vapour pressure increases. At lower temperatures the equilibrium vapour pressure is much less than the pressure of the atmosphere acting on the liquid surface The vapour is therefore not able to push its way through the bulk of the liquid and only a small amount of vapour escapes into the air from the surface. If the temperature is

increased until the vapour pressure becomes equal to the atmospheric pressure, the vapour formed within the liquid can freely rise through the liquid in the form of bubbles and escape into air (Fig. 3.22). When this happens, we say that the liquid is boiling.

Although boiling and evaporation are similar processes, they differ in some respects. While evaporation occurs spontaneously at all temperatures, boiling takes place only at a particular temperature at which the vapour pressure is equal to the pressure of the atmosphere. Another point of difference between evaporation and boiling is that evaporation takes place only at the surface of the liquid whereas boiling involves the formation of bubbles of vapour below the surface of the liquid.

The temperature at which boiling occurs is called the boiling point of the liquid.
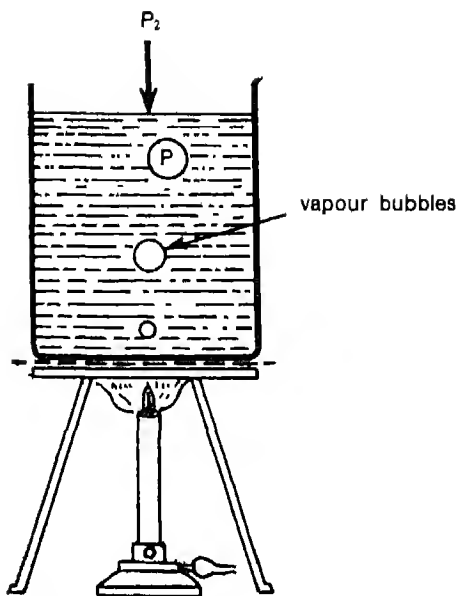
Fig. 3.22 *Boiling of a liquid. at the boiling point of a liquid, vapour pressure of liquid P_1 is equal to pressure on liquid surface, P_2.*

At this temperature, the vapour pressure of the liquid is equal to the atmospheric pressure. T̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ depends upon the atmospheric pressure. The normal boi ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ temperature at which the vapour pressure of a liquid is equal to one atmosphere. Its value can be determined from the vapour pressure-temperature curve (Fig. 3 21). The normal boiling point of water is 100°C, that of ethyl alcohol 76°C, and of diethyl ether 35°C

A liquid may be made to boil at any desired temperature by altering the external pressure. It may be made to boil at a higher temperature than the normal boiling point by increasing the pressure and it may be made to boil at a lower temperature by decreasing the pressure. Substances which decompose at their normal boiling points are usually made to boil under reduced pressure. This principle is used in purifying less stable liquids by distillation under reduced pressure.

Surface tension: Surface tension is another important property of liquids related to the intermolecular forces. A molecule w̲ ̲ within the body of the liquid is attracted equally in all directions by the surrounding molecules. However a molecule on the surface of the liquid is attracted only by molecules below and beside ̲ (Fig 3.23).
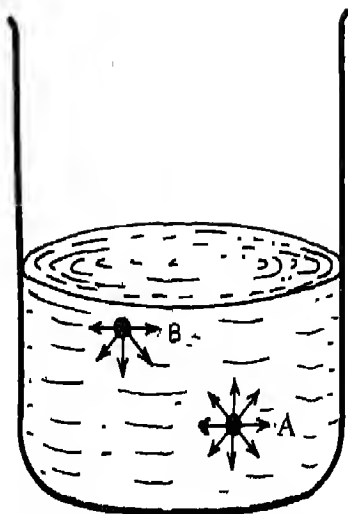
Fig. 3.23   Forces on a molecule at the
surface and in the interior of
a liquid. Arrows show direction
of attractive forces.

This creates an imbalance of forces at the surface. Consequently, molecules at the surface are pulled inward and the surface area of the liquid tends to be minimum. As a result of the tendency to contract, a liquid surface behaves as if it were in a state of tension. This effect is called SURFACE TENSION. Surface tension is a measure of the work that must be done to expand the surface of a liquid by unit area It is expressed in joules/m^2 or newton/m. The surface tension of water is 72.75×10^{-3} newton/m and that of mercury is 475.0×10^{-3} newton/m.

Surface tension accounts for the spherical shapes of liquid drops. It is also responsible for the rise or fall of liquids in capillary tubes. For example, water rises in a capillary tube, while mercury level in a capillary falls. The concave upward meniscus that we observe (when handling liquids in burettes and pipettes) also arises from the surface tension of liquids.

Viscosity. Contrary to solids, liquids flow when a stress is applied. This flow results because intermolecular forces in liquids are relatively small and liquids are largely incompressible. Some liquids like castor oil and honey flow slowly, while some other liquids such as kerosene flow rapidly These differences in flow rates result from a property known as VISCOSITY Viscosity is the resistance in a liquid to flow

The resistance to flow (viscosity) is related to intermolecular forces; stronger the forces, higher is the viscosity When the temperature is raised, the viscosity of liquids decreases. This is because, increase in temperature increases the average kinetic energy of molecules which overcomes the attractive forces between them.

EXERCISES

3 1 Explain the following observations.
   (i) Aerated water bottles are kept under water during summer.
   (ii) Liquid ammonia bottle is cooled before opening the seal.
   (iii) The tyre of an automobile is inflated to lesser pressure in summer than in winter.
   (iv) The size of a weather balloon becomes larger and larger as it ascends into higher altitudes

3 2 A gas is enclosed in a room The temperature, pressure, density, and number of moles respectively are $t°C$, p atm, g cm^{-3} and n moles.
   (i) What will be the pressure, temperature, density and number of moles in each compartment if the room is partitioned into four equal compartments?
   (ii) What will be the values of pressure, temperature, density, and the number of moles in each compartment if the wall between any two compartments, say, 1 and 2, is removed?
   (iii) What will be the values of pressure, temperature, density, and the number of moles if an equal volume of the gas at pressure P and temperature t is let inside the same room?

3.3 Two flasks, A and B, have equal volume. Flask A contains H_2 and is maintained at 300 K while flask B contains an equal mass of CH_4 gas and is maintained at 600 K
   (i) Which flask contains a greater number of molecules? How many times more?
   (ii) In which flask is the pressure greater? How many times greater?
   (iii) In which flask will the molecules move faster?
   (iv) In which flask are the number of collisions with the wall greater?

3.4 The following table shows the effect of changing the pressure on the volume of a sample of gas· The temperature of the gas is held constant.

Pressure (P) (atm)	Volume (V) (L)
1.00	22.4
0.90	24.9
0.85	26.3
0.75	29 9
0.65	40.2
0.55	40.7
0.45	49.8
0 30	74.7
0.20	112

   (i) Plot the following graphs: P vs V, (ii) P vs 1/V, (iii) PV vs P. Interpret each graph in terms of Boyle's Law

(ii) One measurement in the table is wrong Identify it giving reasons.

(iii) Assuming that the pressure values are correct, calculate the volume corresponding to the incorrect point.

3.5 A weather balloon has a volume of 175 L when filled with hydrogn at a pressure of 1.00 atm. Calculate the volume of the balloon when it rises to a height of 2000 m, where the atmospheric pressure is 0.80 atm. Assume that the temperature is constant.

3.6 A sample of helium has a volume of 500 cm^3 at 373 K Calculate the temperature at which the volume will become 260 cm^3. Assume that the pressure is constant.

3 7 A sample of nitrogen gas occupies a volume of 1 000 L at a pressure of 0.500 atm at 40° C Calculate the pressure if the gas is compressed to 0 225 cm^3 at − 6° C.

3.8 (i) How do amorphous solids differ from crystalline solids?
(ii) What are the different types of bonding in solids? Cite at least two examples of each kind of bonding.

3 9 The melting point is a rough measure of the attractive forces in solids Arrange the following solids in order of the increasing strength of attractive forces

	m p (K)
Naphthalene	353
Sodium fluoride	1272
Water (ice)	273
Phosphorus	317
Zinc iodide	719

3 10 Explain the following statements
(i) Sodium chloride pieces are harder than sodium metal
(ii) Copper is ductile and malleable but brass is not.
(iii) The latent heat of fusion of solid carbon dioxide is much less than that of silicon dioxide.
(iv) Water has its maximum density near 277K.
(v) Ice floats on the surface of water near the melting point.

3.11 Draw a diagram to show the structural difference between the three types of cubic crystals.

3.12 What are tetrahedral and octahedral holes in close packed stacks of spheres? What is the importance of these holes in crystals?

3 13 X-rays of wavelength equal to 0 134 nm give a first order diffraction from the surface of a crystal when the value of θ is 10.5° Calculate the distance between the planes in the crystal parallel to the surface examined

3.14 Explain the following·
    (i) The boiling point of a liquid rises on increasing pressure.
    (ii) Drops of liquid assume a spherical shape
    (iii) The boiling point of water (373 K) is abnormally high when compared to that of H_2S (211 2K)
    (iv) The level of mercury in a capillary tube is lower than the level outside when a capillary tube is inserted in mercury.
    (v) Liquids like ether and acetone are kept in cool places.
    (vi) Tea or coffee is sipped from a saucer when it is quite hot

3.15 (i) Which of the liquids in each of the following pairs has a higher vapour pressure (a) alcohol, glycerine; (b) petrol, kerosene, (c) mercury, water?
    (ii) Which one in each of the following pairs is more viscous (a) coconut oil, castor oil; (b) glycerine, kerosene, (c) soft drink, aerated water (soda water)?
    (iii) Separate portions of chloroform and water at the same temperature are poured on your hands The chloroform feels colder. Account for this in terms of attractive forces

3.16 (i) What is the effect of temperature on: (a) density, (b) surface tension, (c) viscosity, (d) vapour pressure of a liquid?
    (ii) What is the effect of pressure on: (a) volume, (b) boiling point, (c) viscosity, of a liquid.

U N I T 4

ATOMIC STRUCTURE

*Atoms contain electrons and electrons
determine chemistry*

OBJECTIVES

In this Unit, we shall learn

*   the explanation of the following:
    Nuclear model of the atom, Bohr model of the atom, quantum
    mechanical model of the atom; uncertainty principle, de Broglie
    relation, Bohr frequency rule, Pauli exclusion principle; orbital
    concept, aufbau principle;

*   to write the electron configuration of atoms;

*   the shapes of s and p orbitals.

THE ATOMIC HYPOTHESIS suggested by Dalton and developed further by Avogadro, Cannizaro and may other chemists of the nineteenth century, regarded an atom as the ultimate particle of matter. It assumed that

  (i)   an atom cannot be subdivided,
  (ii) atoms are neither created nor destroyed during chemical reactions,
  (iii) atoms of the same element are all alike; in particular, all atoms of an element have the same mass,
  (iv) atoms of different elements are not alike, in particular, their masses are different.

Towards the end of the nineteenth century, experimental evidence established that an atom can be subdivided. It is now known that three of the most important constituents of an atom are electrons, protons and neutrons. This observation led to a modification of the Daltonian picture of an atom It also led to a deeper understanding of how the chemical behaviour of an atom is related to its internal structure. The discovery of the electron had profound consequences in physics since it was found that the Newtonian laws of motion do not describe correctly the electron motion. This resulted in the formulation of a new mechanics called quantum mechanics. We will refer to some features of the quantum laws which are necessary to understand the electron arrangement in atoms. This will help us to analyse the chemical behaviour in terms of atomic structure

Let us recall such facts about atomic structure as are common knowledge. An atom consists of a positively charged core called NUCLEUS, which is surrounded by negatively charged particles called ELECTRONS. The nucleus accounts for almost all of the mass of an atom but the space it occupies is negligible compared to the size of the atom The electrons, on the other hand, hardly contribute anything to the mass of an atom but the region of space occupied by them defines the size of the atom. The nucleus of every atom consists of definite number of PROTONS AND NEUTRONS. A proton and a neutron have a similar mass but a proton is positively charged whereas a neutron is uncharged.

It was through brilliant experiments and careful reasoning that the structure of the atom became understood. Let us briefly consider some of the more important experiments. You will learn this topic in greater detail in advanced courses in physics and chemistry.

4.1   CONSTITUENTS OF THE ATOM

The earliest evidence for the electrical nature of matter came from experiments on frictional electricity when it was found that substances like glass or ebonite when rubbed with silk or fur generated electricity. In the 1830 s Michael Faraday showed that chemical changes occur when electricity is passed through an electrolyte Faraday summarised his results in the form of two laws of electrolysis·

(i) If a fixed quantity of charge (i. e., current × time) is circulated through a cell, it produces a fixed amount of particular substance at an electrode.

(ii) The number of moles of various substances liberated at an electrode by fixed quantity of charge are in the ratio of small integers

These statements, known as Faraday's laws of electrolysis, may be illustrated by an example. It is observed that if 96,500 coulombs are passed through a cell containing fused sodium chloride, 1 mole of sodium is deposited at the cathode and 1/2 mole of chlorine (Cl_2) gas is evolved at the anode. These amounts remain fixed as long as the quantity of electricity is 96,500 coulombs. This is in agreement with the first law. The mole ratio is 2·1; this is in agreement with the second law.

The laws of electrolysis are similar to the law of definite proportion and the law of multiple proportion which you have studied in Unit 1. It has been pointed out in Unit 1 that the laws of chemical combination suggest discreteness and identity. Faraday's laws thus imply the discrete (i.e , atomic) nature of electricity. Stoney named the 'atoms' of electricity 'electrons'.

4.1 1   Discovery of the Electron

The reddish orange glow of neon signs is a familiar sight in the cities. A neon sign is a tube filled with neon gas at low pressure. When such a tube, called a GAS DISCHARGE TUBE, is subjected to high voltage, the gas becomes conducting and
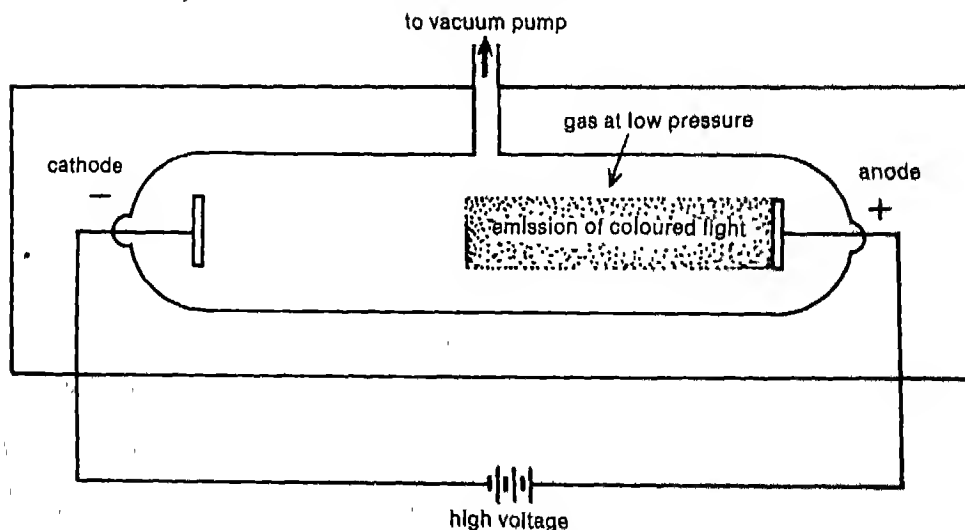
Fig. 4.1 *Discharge tube containing a gas at low pressure. When electric current passes through the gas, it emits coloured light (dotted portion in the figure). The colour depends on the nature of the gas. The remaining region is dark. Cathode rays move from left to right*

begins to glow. The coloured glow results from the emission of light by the atoms of the gas. Experiments with gas discharge tubes in the latter part of the nineteenth century were helpful in identifying the constituents of an atom and they led to the discovery of the electron.

Under ordinary conditions, gases are poor conductors However, if a gas is taken in a sealed tube to which two electrodes are attached (Fig 4 1) and if the gas pressure in the tube is reduced to about 10^- atm, the gas becomes conducting on applying a high voltage (5,000-10,000 volts) to the electrodes. The gas is found to emit light under these conditions. The colour of the light depends upon the nature of the gas The emission of light ceases as the pressure is reduced to about 10^4 atm, but the gas continues to conduct electricity and the glass wall of the tube glows (fluoresces) with a faint greenish light. It was observed that an object placed inside the tube casts a sharp shadow on the wall of the glass tube (Fig. 4 2) This experiment showed that the fluorescence was due to the bombardment of the glass by rays emitted from the cathode and moving in straight lines. These rays were named CATHODE RAYS
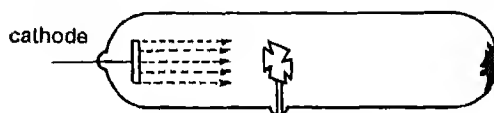
Fig. 4.2 *A sharp shadow of an object is cast by the cathode rays. The same observation in the case of light rays led to the corpuscular (i e., particle) model of light*

The application of electric and magnetic fields deflected the rays in the discharge tube thus establishing that they consisted of charged particles. The direction of deflection showed that the charge was negative (Fig 4.3) By measuring the deflection under the simultaneous influence of electric and magnetic fields, applied perpendicular to each other (Fig.4.4), Sir J.J. Thomson was able to determine the ratio of the charge (e) of the particle to its mass (m). The value of e/m was found to be 1.76×10^8 coulomb/g and the particles were identified as electrons. The ratio e/m was

(a)   (b)
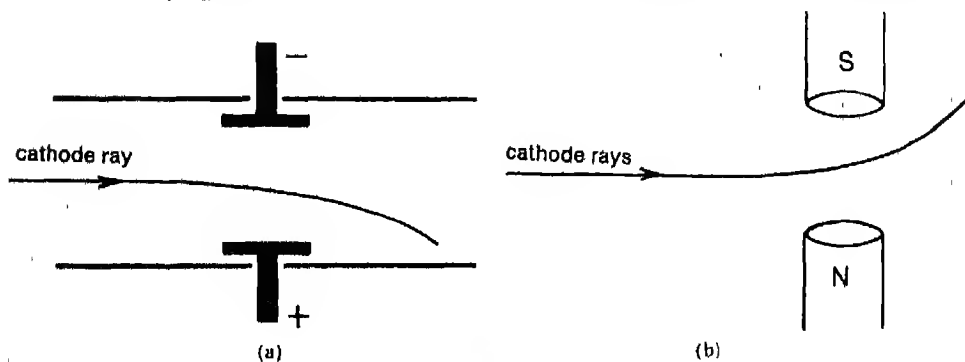
Fig. 4 3 *Bending of cathode rays:* **(a)** *in an electric field,* **(b)** *in a magnetic field*

independent of the nature of the gas in the tube as well as the nature of the cathode, thus showing that electrons are universal constituents of all matter.*

The charge of the electron was measured by Millikan in 1909 as 1.60×10^{-19} coulomb When combined with the value for e/m, this gives the mass of electron as 9.1×10^{-28} g. Fig. 4 5 depicts the set-up used for determining the charge of an electron.
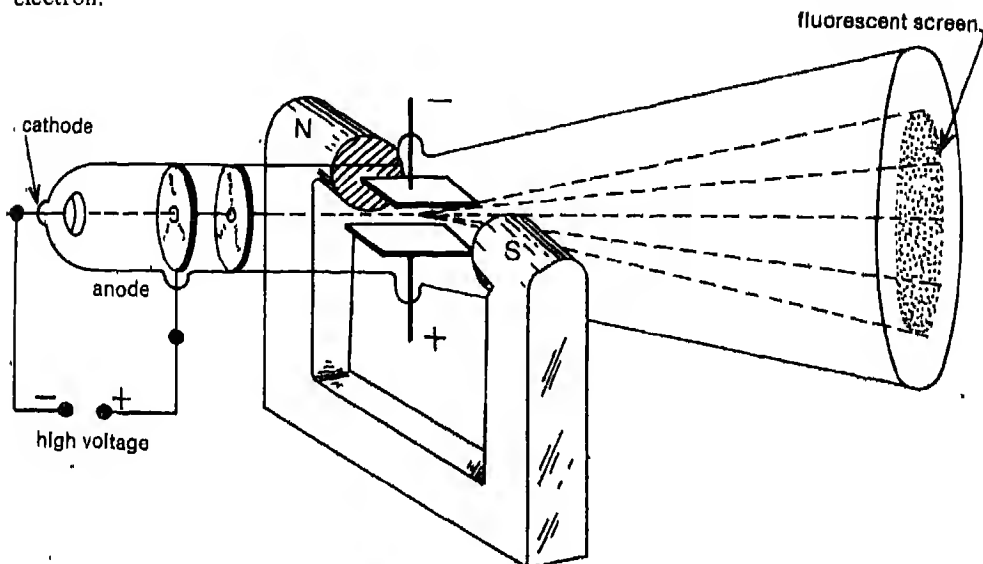
Fig. 4.4 *The apparatus for determining the ratio of charge (e) to mass (m) of electrons. Electrons emitted from the cathode are accelerated by the high voltage between the cathode and the anode. The circular disc after the anode selects the beam moving in a straight line. The beam then passes through electric and magnetic fields which are perpendicular not only to each other but also to the direction of the motion. Their relative strengths and the ratio e/m controls the deflection. Hence, by measurement of deflection and of field strengths, e/m can be calculated*

At moderate pressure, the stream of electrons in a discharge tube collides with neutral atoms or molecules of the gas producing more electrons as well as other particles which move towards the cathode as rays. The deflection of these rays, called canal rays in an electric field shows that they consist of positive ions (Fig. 4.6) The charge and mass of the positive ions are determined in the same manner as described above It is found that positive ions are typically about 2,000 times more massive than electrons; their exact mass depending on the nature of the gas in the tube.

---

* A cathode ray tube is the heart of a television. The movement of cathode rays is controlled by electromagnetic coils When the beam strikes the specially coated screen, it traces a luminescent image.
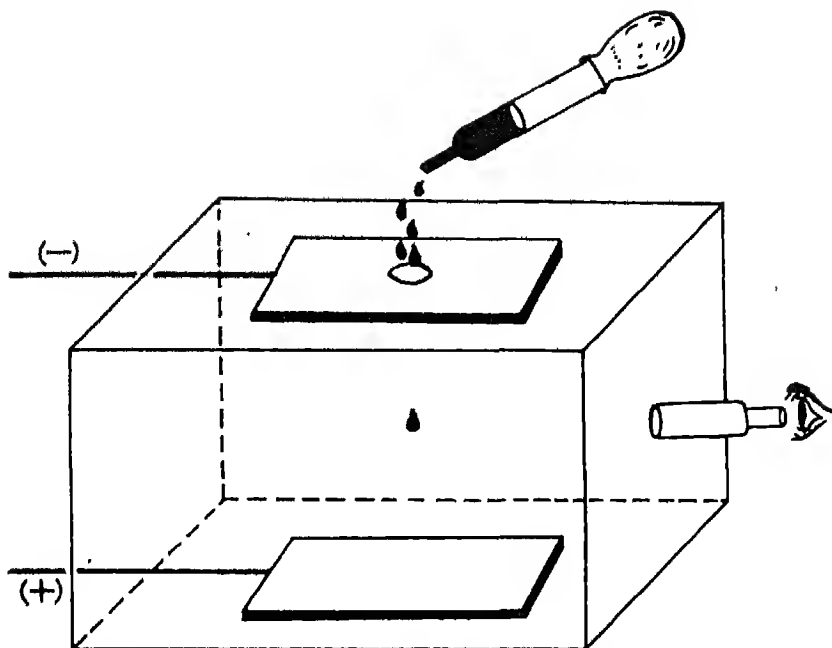
Fig. 4.5 *Milliken's experiment for determination of charge of electron. Oil drops are sprayed and allowed to fall in between two charged plates. A droplet between the plates is observed through a microscope. The negatively charged drops experience gravitational field in the downward direction and electric field in the upward direction. By adjusting the electric field strength, the two forces can be balanced. The drop then either remains stationary or moves with constant speed, (in accordance with the first law of motion)*

The experiments outlined above clearly showed that the atom was divisible, and that it could be split into charged particles Studies on the phenomenon of radioactivity discovered by Becquerel around 1900 also supported this conclusion Radioactivity is the spontaneous emission of radiation by certain elements like radium. Three kinds of radiation named, α, β and γ, have been identified. Their nature has been characterised by methods identical to those used for characterising the cathode
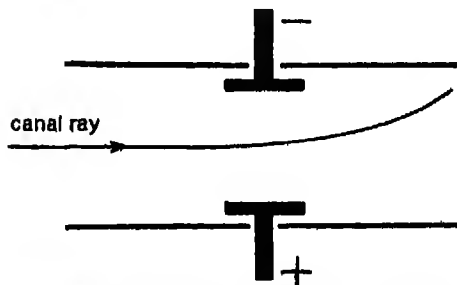
Fig. 4.6 *The direction of deflection of the rays coming from anode shows that they consist of positive particles. These particles have been identified as ions produced by collision of electrons with molecules of the residual gas in the discharge tube. The nature of ions depends upon the nature of the residual gas.*

rays. Alpha rays consist of positively charged He^{2+} particles ($e = 3.20 \times 10^{-19}$ coulomb, $m = 6.6 \times 10^{-24}$g) Beta rays are made up of electrons, while gamma radiation is high-energy electromagnetic radiation having no charge and negligible mass (Fig 4.7).
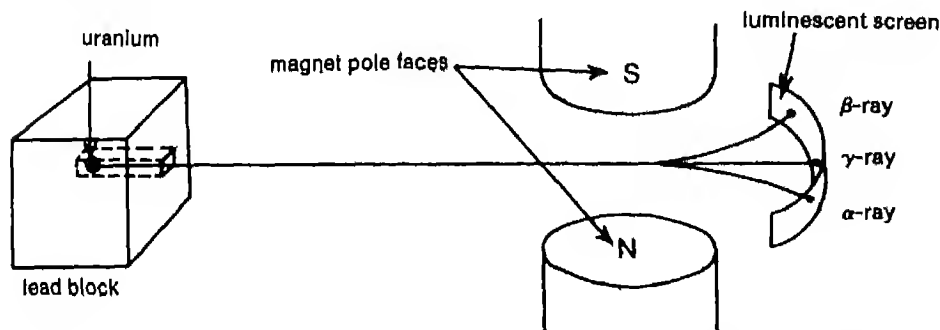
Fig. 4.7 *The α-, β-, and γ-types of radioactivity. It is found that the α-rays consist of He^{2+} ions, the β-rays are made of of electrons, and the γ-rays are high-frequency electro-magnetic radiation.*

4.1.2 Nuclear Model of the Atom

The question that had to be answered next was with regard to the arrangement of the constituent particles inside an atom. J.J. Thomson proposed the first model in which the positive charge was assumed to be smeared over a sphere of radius 10^{-8}cm with the electrons embedded in the sphere (Fig.4.8). The distribution of charge in an atom could be tested by shooting charged particles through thin metal foils and studying the resultant scattering of incident particles which would be governed by the distribution of positive and negative charges inside the atoms. Rutherford carried out this experiment for the first time in 1911 using α-particles (which are doubly charged helium ions, He^{2+}) as incident particles and a gold foil as the target. The scattered particles were counted in different directions. It was observed that a majority of the α-particles went through the foil undeflected while only a small fraction was deflected by small angles. The unexpected feature was that one in about
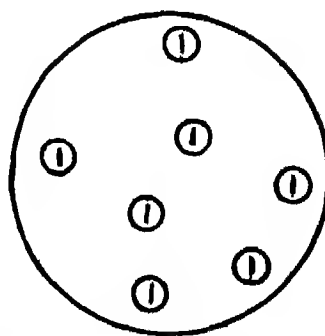
Fig. 4.8 *The Thomson model of an atom. The positive charge was imagined as being spread over the entire atom and the electrons were put in this positive background. This model proved inconsistent with experimental facts.*
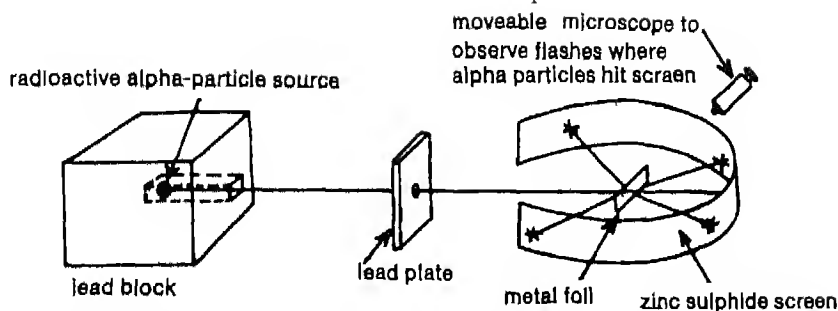
Fig. 4.9 (a) α- particle scattering from metal foils. α-particles are produced by a radioactive source Since lead absorbs α-particles, a lead plate with a hole is used to obtain a beam of α-particles. The scattered particles from the foil are made visible by the tiny flashes which they emit on striking a zinc sulphide screen. A microscope is used to view the flashes.
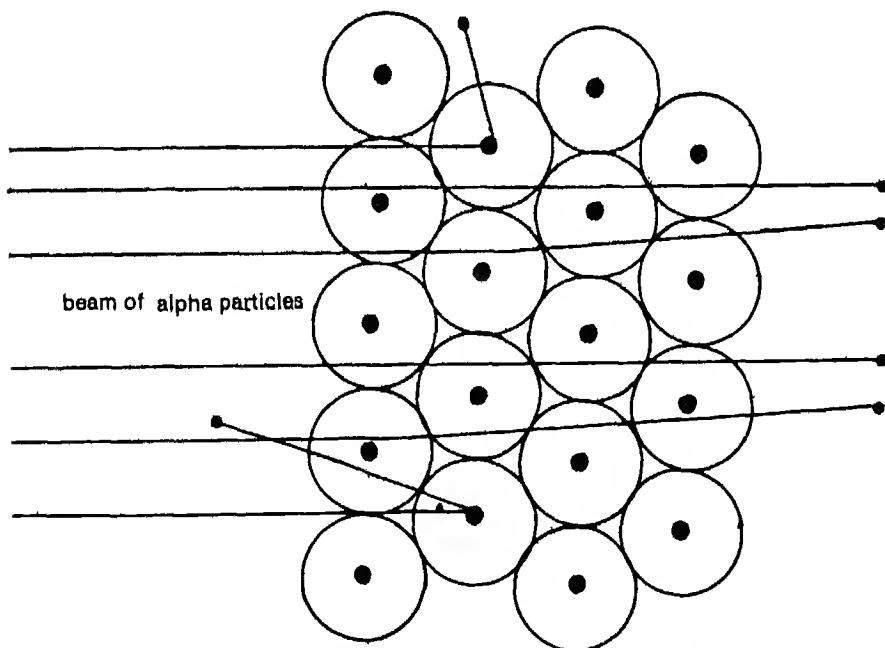
Fig. 4.9 (b) A schematic view of the α-particle scattering by a gold foil. The black dots represent the nuclei of gold atoms. Most of the α-particles pass through with small deflection. A few, however, collide with the nuclei and suffer violent deflections.

20,000 particles came straight back suffering a deflection of 180°. Such violent deflection can arise only if an intense electric field is present inside atoms. Calcula-

tions showed that a positive charge spread over a sphere of radius 10^{-8}cm would be incapable of producing such a field; indeed the radius had to be of the order of 10^{-13}cm to account for the scattering data. Figs 4.9 and 4.10 illustrate the various features of the scattering experiment.

The scattering experiments disproved the Thomson model and led to the nuclear model of the atom in which the positive charge is spread over a sphere of radius 10^{-13} cm—the so-called nucleus—and the electrons are outside the nucleus at a distance of about 10^{-8} cm to account for the typical size of atoms.* It is about 10^{-8}cm to account for the typical size of atoms.* It is possible to calculate the positive charge on the nucleus by counting the number or α-particles scattered in different directions. In this manner it was found that the charges of different nuclei are

(a)
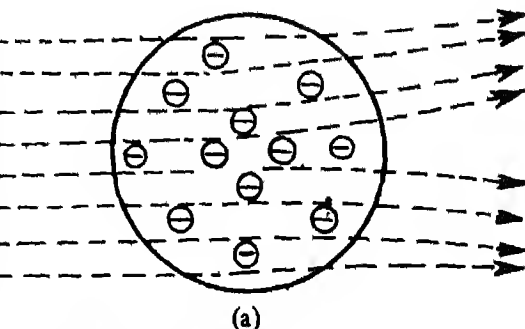
Fig. 4.10 (a) *On the basis of Thomson's model, particles will be deflected through small angles only. This is because the positive charge in the Thomson model is spread uniformly over the entire volume resulting in a relatively weak field.*

always integral multiples of the electron charge but with the opposite sign. Thus, if the electron charge is designated as $-e$, the nucleus of a hydrogen atom is found to have a charge $+1e$, the nucleus of a sodium atom $+11e$, and that of a uranium atom $+92e$. This integer value is called the atomic number and denoted by the symbol Z. Furthermore, since atoms are electrically neutral, one has to assume that there are as many electrons in an atom as the net positive charge on the nucleus. This means that the hydrogen atom has one electron, the sodium atom has 11 electrons and the uranium atom has 92 electrons.

The positive charge of a nucleus is due to the positively charged particles called protons. The proton charge is equal to the electron charge in magnitude, but opposite in sign. This means that the atomic number of a nucleus is equal to the number of protons in that nucleus For example, the nuclei of hydrogen, sodium and uranium atoms have 1, 11 and 92 protons respectively. But whereas the charge of a nucleus is entirely due to the protons, the mass of a nucleus is not due to the protons alone. This is because of the facts that nuclei contain another particle

---

* The atomic size is about hundred thousand (i e, 10^5) times larger than the nuclear size. We can appreciate this difference in sizes by realising that if a cricket ball represents a nucleus, then an atom would be a sphere of about 5 km radius! Atoms are mostly empty space.

(b)
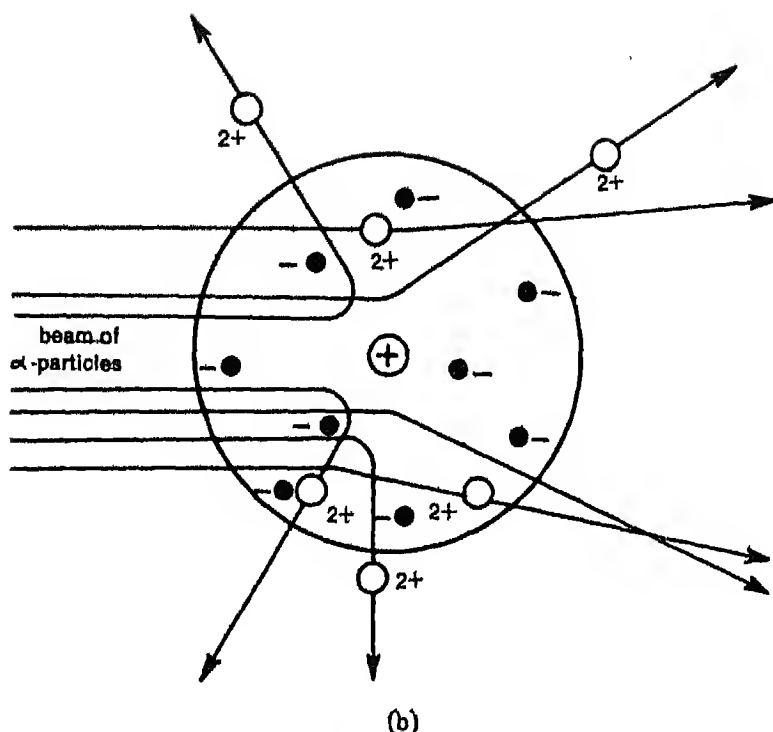
Fig. 4.10 (b) *Results of the scattering experiment which is expected on the basis of Rutherford's model. Experiments support these.*

called neutron which is chargeless and which has a mass very nearly equal to the proton mass. The neutron was identified by Chadwick in 1932. The total number of protons and neutrons in a nucleus, denoted by the mass number (A), determine the nuclear mass. For example, the A values for hydrogen, sodium and uranium nuclei are 1, 23 and 238 respectively. From the definition of A and Z it follows that (A−Z) represents the number of neutrons in a nucleus. Further, since the mass of an electron is negligible compared to that of proton or neutron, the mass of an atom is virtually equal to the nuclear mass.

The atoms of many elements have nuclei which contain the same number of protons but different numbers of neutrons. Such atoms with nuclei having the same value of Z but different values of the mass number, A, are known as the isotopes of the element. Many isotopes were discovered by measuring e/m with help of an instrument called mass spectrometer. For example, hydrogen has the following three isotopes: one isotope with Z = 1, A= 1 (i.e. one proton only), the second isotope with Z = 1, A = 2 (i.e. one proton and one neutron) and the third one with Z = 1,

A = 3 (i.e one proton and two neutrons). The term 'hydrogen' is strictly used only for the first isotope while deuterium (symbol D) and tritium (T) refer to the second and the third varieties respectively. The isotopes of other elements do not have special names; they are indicated by giving the A value on the symbol for the elements. Thus, ^{235}U, ^{238}U, ^{239}U, are the isotopes of uranium.

The Rutherford model of the atom could explain the results of α-particle scattering. However, it had to explain the results of many other experiments before it would be accepted. This topic is discussed in the next section.

4.2 ELECTRONIC STRUCTURE OF ATOMS

The chemical behaviour of an atom is mainly controlled by its electronic structure. The term 'electronic structure' means: (i) number of electrons, (ii) the distribution of these electrons in the space around the nucleus and (iii) the relative energies of these distributions. We have seen that the number of electrons is determined by the atomic number of the elements. To better understand (ii) and (iii) above consider the hydrogen atom, which is the simplest atom. The hydrogen atom contains only one electron. The study of the emission spectrum of light by the hydrogen atom provided the most important clue to its electronic structure In order to understand the emission spectrum we shall briefly examine the nature of light.

4.2.1   Nature of Light and Electromagnetic Waves

The earliest view of light, due to Newton, regarded it as a stream of particles more commonly termed as corpuscles of light. While this view explained the experimental laws of reflection and refraction of light, it failed to account for the phenomena of interference and diffraction. The corpuscular theory was therefore discarded and replaced by the wave theory which considers light to be a form of wave motion. Now, as we know, waves are characterised by wavelength (λ), frequency (ν) and speed of propagation·(c), which are related by the equation

$$\lambda\nu = c$$

The speed of light has been determined and is found to be constant in vacuum. It has the value of 3.00×10^8 meters/sec. The different colours. e.g blue, red, green etc. have different wavelengths or different frequencies. Towards the end of the last century, it was shown that light waves are electromagnetic in nature (i.e. they are oscillations of electric and magnetic fields in space) In other words, light is electromagnetic radiation Various types of electromagnetic radiations having various wavelengths (or frequencies) are now known. They constitute the so-called electromagnetic spectrum.

Different regions of the spectrum are identified by different names. Some examples are· radio frequency region, around 10^6Hz*, used for broadcasting; microwave region (around 10^{10} Hz) used for radar, infrared region (around 10^{13} Hz)

---

*   Hz stands for Hertz. 1 Hz = 1 cycle per second (cps)

which is the heat radiation; and ultraviolet (around 10^{16} Hz) a component of the sun's radiation. The small portion known as the visible spectrum (around 10^{15} Hz) is what is ordinarily called light. It is the only part which our eyes can detect. Special instruments are necessary to detect non-visible types of electromagnetic radiation.

Example 4.1

The Vividh Bharati station of All India Radio, Delhi broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by the transmitter.

Solution

The wavelength, λ, is equal to c/ν where c is the speed of light (electromagnetic radiation in vacuum at the speed of light) and ν is the frequency. Substituting the given values, we have

$$\lambda = \frac{3.00 \times 10^8 \text{ms}^{-1}}{1,368 \text{ kHz}} = \frac{3.00 \times 10^8 \text{ms}^{-1}}{1,368 \times 10^3 \text{s}^{-1}} = 219.3 \text{m}$$

Example 4.2

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express the wavelengths in frequencies (Hz). [nm, the abbreviation for nanometer, is equal to 10^{-9} m.]

Solution

$$\text{Frequency of violet light} = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ms}^{-1}}{400 \times 10^{-9} \text{m}} = 7\,50 \times 10^{14} \text{Hz}$$

$$\text{Frequency of red light} = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ms}^{-1}}{750 \times 10^{-9} \text{m}} = 4\,00 \times 10^{14} \text{Hz}$$

Another property of light is that it is a form of energy. This is quite obvious to all of us who instinctively avoid the heat of sunlight during the summer and welcome it on a cold day. How much energy is carried by light? The answer to the question was given at the beginning of this century by Albert Einstein who based his consideration on the earlier work of Max Planck. He showed that light energy is carried in packets named photons. The energy of a photon is related to the frequency (ν) of the light wave by the equation, $E = h\nu$. Here, h is a universal constant known as Planck's constant. It has the value of 6.63×10^{-34} joules sec or 3.99×10^{-13} kJ sec mol^{-1} This relation, verified experimentally, is valid for all forms of electromagnetic radiation. It shows that the higher the frequency (or the lower the wavelength), the more energetic are the corresponding photons. The photon hypothesis amounts to

saying that light has a corpuscular character. The fact that light exhibits diffraction*
means that light also has a wave character. Thus, experimental facts show that light
has a dual (i.e., particle and wave) character.

4.2.2 Atomic Spectra

When a sample of gas is heated, the atoms and molecules of the gas emit electro-
magnetic radiation of definite frequencies. This set of definite frequencies is referred
to as an emission spectrum of the particular atom or molecule. The characteristic
radiation frequencies that are absorbed by atoms or molecules constitute their
absorption spectra. We shall now briefly discuss some aspects of atomic spectra.

The study of emission spectra was started by Bunsen and by Kirchoff around
1860 The instrument which analyses the wavelength of the emitted radiation is
called a spectroscope Since atoms of different elements were found to emit characte-
ristic sets of wavelengths, emission spectra became useful in chemical analysis to
identify and estimate the elements present in a sample The elements rubidium and
caesium were discovered this way. Other alkali metals like lithium, sodium and
potassium are detected in qualitative analysis by the flame test. A simple experiment
can be carried out at home by heating a copper vessel over a gas flame. A beautiful
green flame, characteristic of copper compounds, will be observed

The most striking feature of atomic spectra is that the emitted (or absorbed)
radiation has very sharp, discrete wavelengths These spectra are, therefore, also
known as line spectra. The hydrogen atom (which contains only one electron) gives
by far the simplest pattern. Balmer showed in 1885 that if spectral lines are
expressed in terms of inverse of wavelength (λ^{-1} or $\bar{\nu}$), then the visible lines of the
hydrogen atom spectra obey the formula:

$$\frac{1}{\lambda} \equiv \bar{\nu} \ (\text{cm}^{-1}) = 109,677 \ (\frac{1}{2^2} - \frac{1}{n^2})$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,.....).

Example 4.3

Calculate the wavelength from the Balmer formula when n = 3.

Solution

$$\bar{\nu} \ (\text{cm}^{-1}) = 109,677 \ (\frac{1}{2^2} - \frac{1}{3^2}] = 109,677 \ (\frac{5}{36})$$

$$\lambda = \frac{1}{\bar{\nu}} \ = \frac{36}{5 \times 109,677} = 656 \ \text{nm}$$

---

* Diffraction is a property of waves in which the waves spread out on encountering an obstruction (e g.,
a small hole) comparable in size to the wavelength. You can observe diffraction by viewing a street
light through a piece of fine cloth; the light will appear blurred due to diffraction. X-ray diffraction is
an important technique for studying crystal structures.

PHOTOELECTRIC EFFECT

When the surface of metal is exposed to light, ejection of electrons from the metal takes place, if the frequency of light is greater than a certain *minimum* value characteristic of the metal This phenomenon is known as the photo-electric effect. A simple example of the effect is emission of electrons by potassium metal. It is observed that violet light is able to eject electrons from potassium but red light (which has lower frequency) has no effect.

Albert Einstein

The explanation for the frequency dependence of the photoelectric effect was given by Albert Einstein in 1905 who was awarded the Nobel Prize for this work. Einstein argued that the wave model of light cannot explain the observed facts. However, if light is regarded as consisting of particles (now named photons) such that the energy (E) of a photon is related to the frequency (ν) by the relation $E = h\nu$, then it is easy to understand the photoelectric effect. Einstein assumed that an electron is ejected from a metal when it is struck by a single photon. It follows that the photon must have sufficient energy to release the electron from the attractive forces of the metal. If the photon has insufficient energy, then it is obvious that it cannot remove any electron no matter how many photons strike the metal. The experiment with the potassium metal referred to above can now be explained as follows. The photon of red light does not have enough energy to remove an electron from potassium. However, a photon of violet light has more energy because of higher frequency and it is therefore able to eject electrons. When the photon strikes the metal, its energy ($h\nu$) is absorbed by the electron causing the photon to disappear. A part of the photon energy is used to free this electron and the excess shows up as the kinetic energy of the released electron. In equation form, we have the result

$$h\nu = W + KE$$

where $h\nu$ is the energy of the photon, W is the energy required to overcome the attractive forces on the electron in the metal, and KE is the kinetic energy of the free electron. An application of this equation is given in Example 4.4

Example 4.4

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^5 J\ mol^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

Solution

The energy (E) of a 300 nm photon is given by

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} Js) (3.00 \times 10^8 m)}{300 \times 10^{-9} m}$$

$$= 6.63 \times 10^{-19} J$$

The energy of 1 mol of photons $= 6.63 \times 10^{-19} J \times 6.022 \times 10^{23}$

$$= 3.99 \times 10^5\ J\ mol^{-1}$$

The minimum energy needed to remove a mole of electrons from

$$sodium = (3.99 - 1.68)\ 10^5\ J\ mol^{-1}$$

$$= 2.31 \times 10^5\ J\ mol^{-1}$$

The minimum energy for one electron $= \dfrac{2.31 \times 10^5 J}{6.022 \times 10^{23}\ electrons}$

$$= 3.84 \times 10^{-19} J \cdot per\ electron$$

This corresponds to the wavelength 518 nm (i.e. green light).

Soon afterwards, Rydberg showed that the more general expression,

$$\bar{\nu} \text{ (in cm}^{-1}) = 109{,}677 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where n_1 and n_2 are integers, such that $n_1 > n_2$, can reproduce all the observed spectral lines of the hydrogen atom. (The Balmer formula gives only the spectral lines in the visible region.) The constant 109,677, which has the dimension of reciprocal length and is characteristic of the hydrogen atom, is called the Rydberg constant.

Atomic Spectra and the Rutherford Model: As stated earlier, Rutherford established on the basis of the scattering experiments, that an atom consists of a heavy positively charged nucleus with lighter negatively charged electrons moving outside. This model of the atom is like a small-scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. Furthermore, the coulomb force (q_1q_2/r^2, where q_1 and q_2 are the charges and r is the distance of separation of the charges) between and electron and the nucleus is mathematically similar to the garvitational force ($-Gm_1m_2/r_2$) between a planet and the sun. When the Newtonian theory was applied to the solar system, it showed that the planets describe well-defined orbits around the sun which persist forever. The theory could also precisely calculate the planetary orbits and these are in impressive agreement with experimental measurements. The similarity between the solar system and the nuclear model suggests that electrons should move around the nucleus in well-defined calculable orbits. However, there arises a difficulty. In following an orbit, a body undergoes acceleration. (Even if a body is moving with constant speed in an orbit, it must accelerate because of changing direction.) So an electron, describing planet-like orbits, will accelerate. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation. (This feature does not exist for planets since they are uncharged.) Therefore, an electron in orbit will emit radiation; the energy carried by radiation coming from electron motion. The orbit will thus continue to shrink Calculations show that it should take an electron only 10^{-8}s to spiral into the nucleus Thus, the Rutherford model cannot explain the stability of an atom if the motion of the electron is described on the basis of Newton's laws of motion and the electromagnetic theory. Since the latter also predicts that the frequency of radiation of a charged body is equal to the frequency of revolution, it follows that as the electron orbit continuously changes so would its frequency of revolution The atomic spectra should have been, therefore, continuous rather than discrete This is in disagreement with the observed facts. The essence of the problem can then be summarised as follows Scattering

experiments require a nuclear atom, but if electron motion is calculated using Newtonian laws, then the Rutherford atom can neither have stability nor exhibit line spectra. Obviously some new ideas were required to solve the puzzle. Since the hydrogen atom contains only one electron, and is therefore the simplest atom, it was natural to tackle this problem first.

4.2.3 Bohr's Model of the Hydrogen Atom

The first attempt to explain the structure of the hydrogen atom was made by the famous Danish physicist, Niels Bohr in 1913. Bohr introduced two novel ideas. The first one is that an electron in an atom is allowed only certain stationary states. In these states, an electron emits no radiation and therefore its energy remains fixed. The term stationary does not mean that the electron is stationary but only that the electron energy is stationary, i.e, not changing with time. Such an idea was introduced because it was in accord with the known stability of atoms.

The energies of different stationary states vary. Under certain conditions, an electron makes a transition from a state of higher energy to a state of lower energy. The difference in energy is then given out in the form of radiation. The Bohr rule relating the energy difference to the frequency of radiation has the form

$$E_2 - E_1 = h\nu$$

where E_2 is the energy of the higher state, E_1 the energy of the lower state, ν the frequency of radiation emitted and h Planck's constant. Bohr was led to this idea by the two features of the spectrum of hydrogen atom mentioned earlier. If E_2 and E_1 can only have some special values, then it follows that ν can also have only special, and not all, values. Further, if the energies are characteristic of an atom, so will the emitted frequencies be.

From Bohr's model one can calculate the energies of various stationary states in the hydrogen atom. The energy (E_n) of each stationary state, also called an energy level, is given by the expression

$$E_n = \frac{-1312}{n^2} \text{ kJ mol}^{-1}$$

where n is the quantum number of the energy level and has the values 1,2,3,..... Thus for each value of n, there exists a possible energy level for the electron, the value of the energy being given by the above expression. Since the lowest permissible value of n is 1, the lowest energy level—called the ground state—has a value of -1312 kJ mol^{-1}. The negative sign has arisen because the zero energy state is taken as when the hydrogen atom is ionised (i.e. the electron is far removed from the nucleus). In other words, compared to the ionised atom, the electron in a hydrogen atom has less energy, i.e., the atom is more stable. If we wish to ionise a hydrogen

atom, we will have to supply $+$ 1312 kJ mol^{-1} of energy. The ionisation energy of a hydrogen atom is therefore $+$ 1312 kJ mol^{-1}.

The energy level formula derived by Bohr, correctly reproduces the hydrogen atom spectra. Example 4.5 shows this by using the Bohr formula.

Example 4 5

Calculate the wavelength of radiation emitted when an electron in a hydrogen atom makes a transition from an energy level with n = 3 to a level with n = 2.

Solution

The energy levels for n = 2 and n= 3 are

$$E_2 = -\frac{1312}{4} \text{ kJ mol}^{-1}; \quad E_3 = -\frac{1312}{9} \text{ kJ mol}^{-1}$$

$$\Delta E = E_{\text{initial}} - E_{\text{final}} = -1312\left(\frac{1}{9} - \frac{1}{4}\right)$$

$$= 180.2 \text{ kJmol}^{-1}$$

To get the energy emitted by *one* atom, the difference in energy obtained above for *one* mole is divided by Avogadro's number, i e ,

$$\Delta E \text{ (per atom)} = \frac{182.2}{6\ 02 \times 10^{23}} \text{ kJ atom}^{-1}$$

$$= 3.03 \times 10^{-19} \text{ J atom}^{-1}$$

This energy is carried by one photon so this value is also the energy of the photon To obtain the wavelength of the photon, we use the well known relations

$$E = h\nu \text{ and } \nu = \frac{c}{\lambda}$$

$$\text{or } \lambda = \frac{hc}{E}$$

Substituting for $h = 6\ 63 \times 10^{-34}$ Js
and $c = 3.00 \times 10^{8}$ ms^{-1}
We get

$$\lambda = \frac{(6.63 \times 10^{-34}) \times (3.00 \times 10^{8})}{3.03 \times 10^{-19}}$$

$$\lambda = 6.56 \times 10^{-7} \text{m}$$
$$\lambda = 656 \text{ nm}$$

(in agreement with the vlaue obtained earlier.)

The idea that the energy of an electron in an atom cannot have any arbitrary value but only certain characteristic values is commonly expressed by the statement

that the electron energy is quantised. 'Quantisation' means that a quantity does not vary continuously. Let us take two familiar examples to clarify this point. The indicator on the dial of a car moves continuously because the speed of a car can have any value But the fare meter of a taxi changes discontinuously because the fare can only have values in multiples of 20 paise. One would say that the fare is quantised but not the speed Quantisation of energy in atoms and molecules is a firmly established fact now because it has been possible to verify by direct experiments.

Bohr's theory worked perfectly for the hydrogen atom but it failed to predict spectra of more complicated atoms. It was clear that though Bohr's ideas were an important advance, they were not adequate to solve the problem of the electronic structure of the atoms.

4 2.4 Quantum Mechanical Model of the Atom

The French physicist, Louis de Broglie, made a bold suggestion in 1924 He argued that since light has been found to have a dual character, i.e., it behaves like waves and like particles, it is possible that electrons also possess a dual character. De Broglie, further proposed from his mathematical theory that the wavelength (λ) should be related to the momentum (p) by the equation

$$\lambda = h/p$$

where h is Planck's constant. De Broglie's idea was soon verified experimentally by observing diffraction effects with an electron beam This fact is put to use in making an electron microscope which is based on the wave-like behaviour of electrons just as an ordinary microscope utilises the wave nature of light An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

The wave nature of an electron puts some restriction on how precisely its position can be determined. Analysis of this question led the great German physicist, Werner Heisenberg, to state in 1927 his famous UNCERTAINTY PRINCIPLE. According to this principle, it is not possible to determine simultaneously the position and the momentum of a body to an arbitrary accuracy. The main fault in the Bohr model should now be clear. In assigning precisely defined orbits, it violates the uncertainty principle. A proper understanding of the atomic structure is not possible without taking into account the wave nature of the electron and of the uncertainty principle.

Probability Picture of Electrons: Whenever we find that an exact and precise statement is not possible, we adopt less exact ways for describing the situation. For example, it is not possible to predict the outcome of say, a test match in advance. One cannot say for sure which team will win or whether the match would end in a

draw. However, from the current and the past form of the players, it is possible to anticipate which team is more likely to win. Similarly, although we can say without hesitation that the sun will rise in the east tomorrow morning—the weather report even gives the exact time of sunrise—we are unable to predict correctly whether it will rain tomorrow or not. The weather report, therefore, only states whether there is a chance of rain or not. Consider yet another example. When a coin is tossed, it may land 'head' or 'tail'. An exact prediction is impossible because both are equally probable. If we toss a coin hundred times, we expect that there will be about fifty 'heads' and fifty 'tails'. In other words, the probability of getting 'heads' and 'tails' is equal. Alternately, one can say that the probability of each event is fifty per cent. It should be noted that this statement does not mean that in hundred tosses, we *must* get fifty 'heads'. It only means that fifty 'heads' are even more likely. Seventy five 'heads' are unlikely, hundred 'heads' are even more unlikely, but neither of the latter possibilities is impossible. Probabilistic estimates provide the best possible description of a situation which cannot be exactly described.

Let us now return to the problem of the electron in the hydrogen atom. In Bohr's model, the electron was supposed to describe a variety of orbits. In each orbit, the electron had a fixed and characteristic value of energy. A precise description of the electron position, as implied in the orbit idea, being impossible, one adopts the probabilistic description in which the relative probabilities of finding an electron at different points in the space around the nucleus are given Such probability distributions in space are called ORBITALS. In an orbital, there are regions of higher probability where the electron is more likely to be found and there are regions of lower probability where the chances of finding the electron are less For different kinds of orbitals one can say whether, on an average, the electron will be closer or farther from the nucleus, whether it will more likely be along a particular direction and so on. In each orbital the electron has a definite energy. The energy is lower if the orbital is concentrated near the nucleus. This is because the electron is more strongly attracted when it is close to the nucleus. The change in energy from one orbital to another is not continuous but discontinuous (i.e., energy is quantised).

Orbitals and Quantum Numbers: A large number of electron orbitals are possible in a hydrogen atom. Orbitals can be distinguished in a qualitative manner by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly, shape and orientation mean that electron distribution has more probability along certain directions and less along certain others.

Orbitals are precisely distinguished by what are known as quantum numbers. It can be shown that each orbital is designated by three quantum numbers labelled as n, *l* and m. The first one, n, is called the principle quantum number and it gives an idea of the size. Large n means a large size. The quantum number, *l*, gives the shape,

and m, the orientation of the orbital. The quantum numbers n, ℓ and m cannot have arbitrary values. They can only have specific values as shown below:

n = 1,2,3,...   (only positive integers)
ℓ = 0,1,2,...,(n−1)   (zero and positive integers up to n− 1)
m = −ℓ, −ℓ+1,...,0,...,ℓ−1, ℓ, (2ℓ+1 vlaues)

We can work out the permitted combinations from these rules. For example, for n = 1, there is only one choice with ℓ = 0. For n = 2, there are two choices ℓ = 0 and 1. For n = 3, one can have ℓ = 0, 1 or 2 and so on. It can be shown that for a given ℓ value there are 2ℓ+1 choices. These are associated with the quantum number m. For a given value of ℓ, m can vary between +ℓ to −ℓ through zero, thus giving rise to the 2ℓ+1 choices mentioned earlier. Thus we find that if ℓ = 0, m = 0 and if ℓ = 1, m = +1, 0, −1. Orbitals with ℓ values of 0, 1, 2, and 3 are referred to as s, p, d and f orbitals respectively.

We designate different orbitals as follows:

n = 1, ℓ = 0 : 1s orbitals (where the prefix 1 is the n vlaue)
n = 2, ℓ = 0 : 2s orbitals (where the prefix 2 is the n vlaue)
n = 2, ℓ = 1 . 2p orbitals (where the prefix 2 is the n value)

The various energy levels as defined by these quantum numbers are shown in Fig. 4.11. In the case of the 2p orbital, there can be three possible m values (+1, 0, −1) indicated by numerical subscripts (p_{+1}, p_0, p_{-1}) or alphabetical subscrips (p_x, p_y, p_z). Thus there are three 2p orbitals, each along the cartesian axes.

In the same manner, it can be shown that there are nine orbitals for the n = 3 case; one of the s type, three of the p type and five of the d type. The spatial distribution of 1s and 2p orbitals are shown in Fig. 4 12
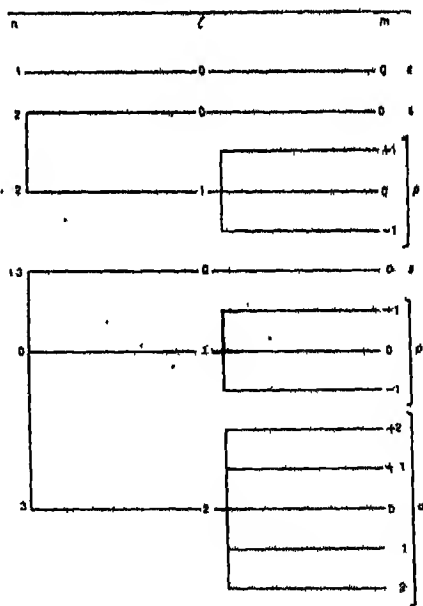
Fig. 4.11   *The permissible combination of n, l, and m*

1 s orbital
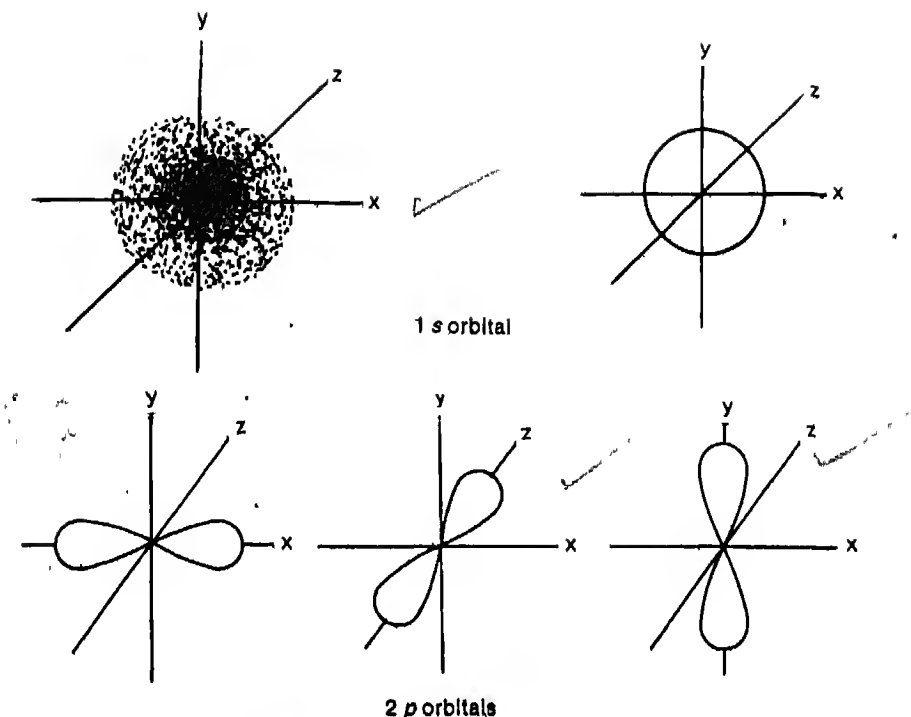
2 p orbitals

Fig. 4.12 *The 1s and 2p orbital diagrams*

We see that s orbital is spherical while the p orbitals are dumb-bell shaped. That is, in an s orbital the electron distribution is symmetric (around the nucleus) in all directions but in p orbitals, distribution is along the axes. The various orbitals have different energies and their arrangement according to increasing energy is shown in Fig. 4.13. The energy level scheme given in this figure is applicable to atoms containing more than one electron, i.e. to all atoms except the hydrogen atom*.

Apart from the spatial distribution given by the orbital, an electron has an additional characteristic called the spin. In the Bohr model, spin was introduced by analogy to the planetary case. The earth moves in an orbit around the sun, but at the same time, it spins around an axis. (The orbit motion controls the duration of the year while the spinning motion regulates the duration of the day.) In the same manner, an electron was thought to be spinning while moving in an orbit. The spin

---

* In the hydrogen atom, all the orbitals having the same principal quantum number, have the same energy. Thus, 2s and 2p have equal energy; 3s, 3p and 3d have equal energy, 4s, 4p, 4d and 4f have equal energy and so on

is also quantised and designated by an additional quantum number, called the spin quantum number, s, which can have only two values, $+1/2$ and $-1/2$ which can be approximately thought of as clockwise and anticlockwise rotation about an axis.
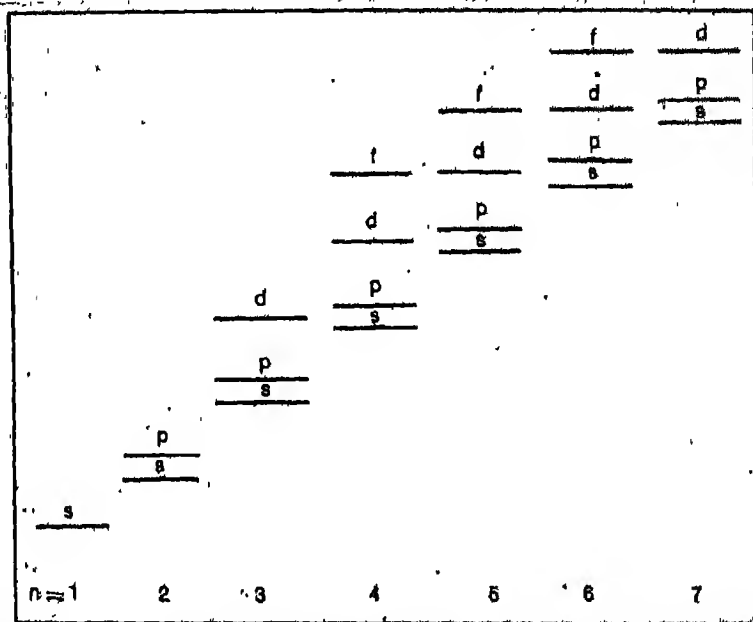
Fig. 4.13 *Relative energies of the various orbitals in an atom. The energy is increasing along the vertical axis. The diagram gives the order of filling of orbitals in neutral atoms; electrons enter the first available orbital of lowest energy.*

Although later developments showed the orbit picture of the electron spin to be wrong, the idea of the spin quantum number itself is correct. However, we no longer think of the electron spin as due to axial rotation but treat it as an intrinsic characteristic of the electron connected with its magnetic behaviour. (The two values that the spin quantum number can have are symbolically indicated as ↑ and ↓, called up-spin and down-spin respectively)

The three quantum numbers labelling an orbital can be used equally well to label the electron in the orbital. In addition, the electron has also a spin quantum number. Thus, we find that each electron in an atom is identified and designated by four quantum numbers. The four quantum numbers serve as the signature of an electron. Just as the signature of a person is unique and is therefore used to identify an individual, a set of four quantum numbers is also unique and helps to characterise an electron (Fig. 4.14). The three quantum numbers n, ℓ, m tell us about its spatial
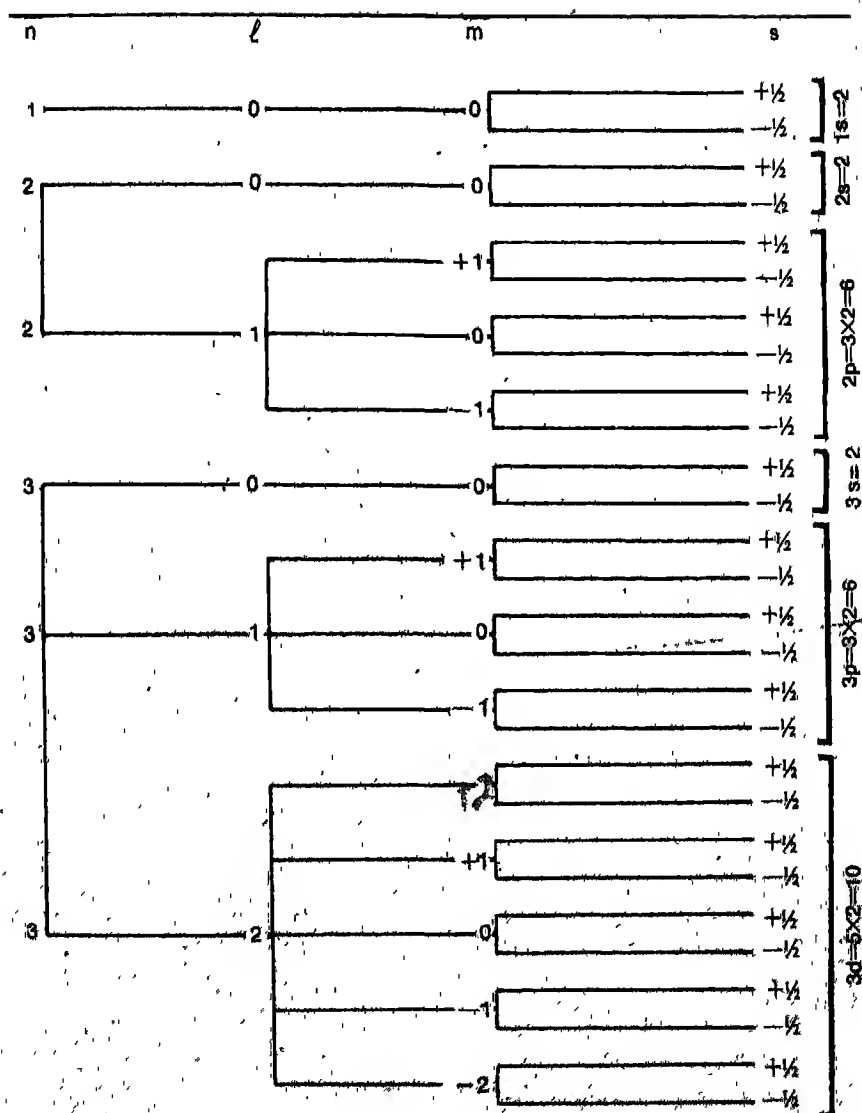
Fig. 4.14 *Permissible combinations of n, l, m, and s. The maximum number of electrons which s, p and d sub-shells can accommodate, is also shown on the right.*

distribution while the spin quantum number indicates the spin orientation.

The orbitals possessing the same principal quantum number, n, are said to belong to a shell. Shells are commonly designated by capital letters starting with K. Thus the shell corresponding to n = 1 is called K shell while those corresponding to n = 2 and n = 3 are called L and M shells respectively. Orbitals with the same value of n but diferent values of ℓ are referred to as subshells. For example, the L shell has two subshells consisting of the s subshell for $\ell = 0$ (containing the 2s orbital) and the p subshell for $\ell = 1$ (consisting of the three 2p orbitals).

We need one more rule before we can proceed to discuss the electronic structure of atoms. The rule was first given by the Austrian scientist, Wolfgang Pauli. It is known as the Pauli exclusion principle. It states that no two electrons in an atom can have the same set of four quantum numbers. If one electron in an atom has some particular value for the four quantum numbers, then all the other electrons in that atom are excluded from having the same set of values, hence the name exclusion principle. It follows that any two electrons of an atom must differ in at least one quantum number.

Since the electrons in an orbital must have the same n, ℓ, m, quantum numbers, it also follows that an orbital can at the most contain two electrons provided their spin quantum numbers are different (i.e., one has an up-spin clockwise and the other a down-spin anticlockwise). The combination of up and down spins is commonly called as pairing of spins. The Pauli principle is often stated in an alternate form as 'An orbital can contain only two electrons' ; it being understood that the two electrons are spin-paired (two different spin quantum numbers). As a consequence of this principle, two is the maximum number of electrons permitted in an s orbital, six in three p orbitals and ten in the five d orbitals. This can be seen clearly from Fig. 4.14.

4.2.5 Electron Configuration of Atoms (Aufbau Principle)

Deducing the electronic configuration of any atom is now an easy matter. We start filling the orbitals beginning with the lowest energy orbital and keeping in mind the Pauli exclusion principle. An orbital filling diagram which will help in writing the electronic configuration of any element is given in Fig. 4.15. The sequence of filling the orbitals can also be obtained from the following two rules:

1. Orbitals fill in the order of increasing n + ℓ. This means that between 3d and 4s, the 4s (n+ ℓ = 2 + 2 = 4) will fill before 3d (n + ℓ = 3 + 2 = 5).

2. If two orbitals have the same n + ℓ, the one with the lower n will be filled first. Thus, between 2p (n+ ℓ = 2+ 1 = 3) and 3s (n+ ℓ = 3+ 0 = 3), 2p will fill before 3s.

Let us now apply these considerations to derive the electronic configuration of different atoms.

The hydrogen atom has only one electron which goes in the orbital with lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is therefore $1s^2$. The third electron of lithium (Li) is not allowed in the 1s orbital because of the Pauli principle. It therefore takes the next available choice, namely the 2s orbital. The electronic configuration of lithium is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of the beryllium (Be) atom is, therefore, $1s^2 2s^2$ (see Table 4.1 for the electronic configuration of elements).

In the next six elements—boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$)—the 2p orbitals get progressively filled. This process is completed with the neon atom. The electronic configurations of the elements from sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$) follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and one electrons respectively.
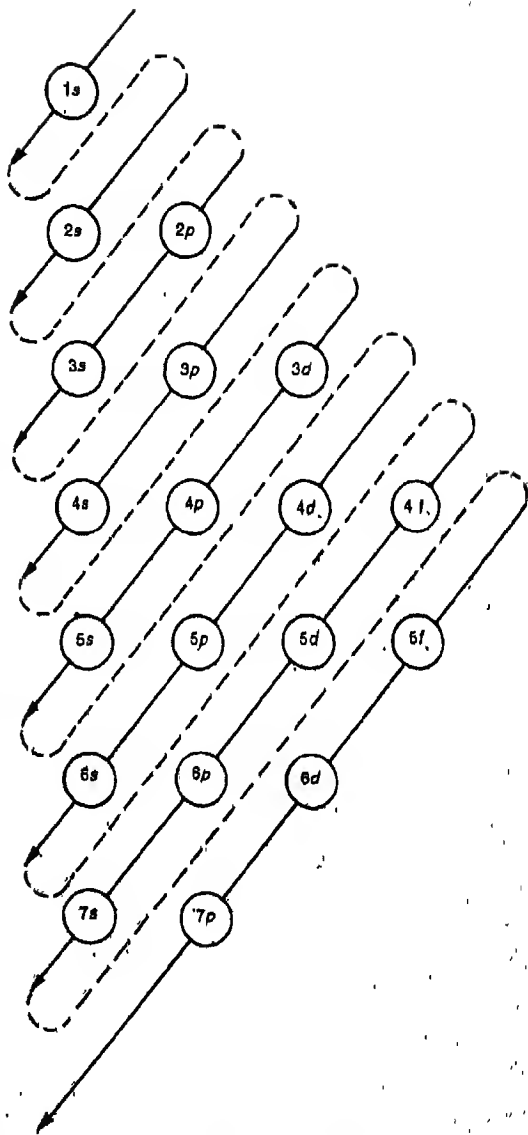
Fig. 4.15 A memory aid for filling the orbitals according to the aufbau principle

A new feature shows up beginning with scandium (Sc). The $3d$ orbital, being lower in energy than $4p$, is filled first. Consequently, in the next ten elements,—scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn)—the five $3d$ orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in $3d$ orbitals rather than four and nine as their positions would have indicated (with one electron in the $4s$ orbital). The reason is that fully filled orbitals and half-filled orbitals have extra stability (i e., lower energy). Thus the p^3, p^6, d^5, d^{10}, f^7 and f^{14} configurations, which are either filled or half-filled, are more stable. Chromium and copper, therefore, adopt the d^5 and d^{10} configurations in preference to the d^4 and d^9 configurations.

With the saturation of the $3d$ orbitals, the $4p$ orbitals start getting filled from gallium (Ga) to krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the $5s$, $4d$ and $5p$ orbitals is similar to that of $4s$, $3d$ and $4p$ discussed above. Then comes the turn of the $6s$ orbital. In caesium (Cs) and barium (Ba), this orbital contains one and two electrons respectively. Then from lanthanum (La) to mercury (Hg) the filling up of electrons takes place in $4f$ and $5d$ orbitals. After this, filling up of $6p$, then $7s$ and finally $5f$ and $6d$ orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially.

Statements like "an orbital is getting filled" or "electrons occupy certain orbitals" should not be taken to mean that orbitals are some kind of containers. What these statements mean is the following. The shape and size of electron distribution is described by orbitals which are labelled by the quantum numbers. Because each distribution has definite energy, the orbitals can be arranged in terms of increasing energy. Every electron in an atom would like to have the distribution (i.e., orbital)

TABLE 4.1

Electronic Configurations of Elements

Atomic Number	Element	Electron configuration	Atomic Number	Element	Electron configuration
1	H	$1s^1$	53	I	$-4d^{10}5s^25p^5$
2	He	$1s^2$	54	Xe	$-4d^{10}5s^25p^6$
3	Li	$He2s^1$	55	Cs	$Xe6s^1$
4	Be	$-2s^2$	56	Ba	$-6s^2$
5	B	$-2s^22p^1$	57	La	$-5d^16s^2$
6	C	$-2s^22p^2$	58	Ce	$-4f^26s^2$
7	N	$-2s^22p^3$	59	Pr	$-4f^36s^2$
8	O	$-2s^22p^4$	60	Nd	$-4f^46s^2$

TABLE 4.1 *(Contd)*

Atomic Number	Element	Electron Configuration	Atomic Number	Element	Electron Configuration
9	F	$-2s^22p^3$	61	Pm	$-4f^56s^2$
10	Ne	$-2s^22p^6$	62	Sm	$-4f^66s^2$
11	Na	Ne $3s^1$	63	Eu	$-4f^76s^2$
12	Mg	$-3s^2$	64	Gd	$-4f^75d^16s^2$
13	Al	$-3s^23p^1$	65	Tb	$-4f^96s^2$
14	Si	$-3s^23p^2$	66	Dy	$-4f^{10}6s^2$
15	P	$-3s^23p^3$	67	Ho	$-4f^{11}6s^2$
16	S	$-3s^23p^4$	68	Er	$-4f^{12}6s^2$
17	Cl	$-3s^23p^5$	69	Tm	$-4f^{13}6s^2$
18	Ar	$-3s^23p^6$	70	Yb	$-4f^{14}6s^2$
19	K	Ar$4s^1$	71	Lu	$-4f^{14}5d^16s^2$
20	Ca	$-4s^2$	72	Hf	$-4f^{14}5d^26s^2$
21	Sc	$-3d^14s^2$	73	Ta	$-4f^{14}5d^36s^2$
22	Ti	$-3d^24s^2$	74	W	$-4f^{14}5d^46s^2$
23	V	$-3d^34s^2$	75	Re	$-4f^{14}5d^56s^2$
24	Cr	$-3d^54s^1$	76	Os	$-4f^{14}5d^66s^2$
25	Mn	$-3d^54s^2$	77	Ir	$-4f^{14}5d^76s^2$
26	Fe	$-3d^64s^2$	78	Pt	$-4f^{14}5d^96s^1$
27	Co	$-3d^74s^2$	79	Au	$-4f^{14}5d^{10}6s^1$
28	Ni	$-3d^84s^2$	80	Hg	$-4f^{14}5d^{10}6s^2$
29	Cu	$-3d^{10}4s^1$	81	Tl	$-4f^{14}5d^{10}6s^26p^1$
30	Zn	$-3d^{10}4s^2$	82	Pb	$-4f^{14}5d^{10}6s^26p^2$
31	Ga	$-3d^{10}4s^24p^1$	83	Bi	$-4f^{14}5d^{10}6s^26p^3$
32	Ge	$-3d^{10}4s^24p^2$	84	Po	$-4f^{14}5d^{10}6s^26p^4$
33	As	$-3d^{10}4s^24p^3$	85	At	$-4f^{14}5d^{10}6s^26p^5$
34	Se	$-3d^{10}4s^24p^4$	86	Rn	$-4f^{14}5d^{10}6s^26p^6$
35	Br	$-3d^{10}4s^24p^5$	87	Fr	Rn$7s^1$
36	Kr	$-3d^{10}4s^24p^6$	88	Ra	$-7s^2$
37	Rb	Kr$5s^1$	89	Ac	$-6d^17s^2$
38	Sr	$-5s^2$	90	Th	$-6d^27s^2$
39	Y	$-4d^15s^2$	91	Pa	$-5f^26d^17s^2$
40	Zr	$-4d^25s^2$	92	U	$-5f^36d^17s^2$
41	Nb	$-4d^45s^1$	93	Np	$-5f^46d^17s^2$
42	M	$-4d^55s^1$	94	Pu	$-5f^67s^2$
43	Tc	$-4d^55s^2$	95	Am	$-5f^77s^2$
44	Ru	$-4d^75s^1$	96	Cm	$-5f^76d^17s^2$
45	Rh	$-4d^85s^1$	97	Bk	$-5f^97s^2$
46	Pd	$-4d^{10}$	98	Cf	$-5f^{10}7s^2$
47	Ag	$-4d^{10}5s^1$	99	Es	$-5f^{11}7s^2$
48	Cd	$-4d^{10}5s^2$	100	Fm	$-5f^{12}7s^2$
49	In	$-4d^{10}5s^25p^1$	101	Md	$-5f^{13}7s^2$
50	Sn	$-5d^{10}5s^25p^2$	102	No	$-5f^{14}7s^2$
51	Sb	$-4d^{10}5s^25p^3$	103	Lr	$-5f^{14}6d^17s^2$
52	Te	$-4d^{10}5s^25p^4$			

corresponding to the lowest energy. But the Pauli principle prevents this by allowing only two electrons per orbital. We, therefore, try to find at each stage which orbital with the lowest energy is available. This principle has been followed in arriving at the electronic configuration of the various atoms. The principle is known as the Aufbau principle (*aufbau* in German means 'building up').

What is the utility of knowing the electron configuration? You will see that the modern approach to chemistry depends almost entirely on electron distributions to understand and explain chemical behaviour For example, questions like why some elements are metals while others are non-metals; why elements like helium, neon, argon are not reactive but elements like the halogens are reactive, find a simple explanation from the electronic configuration point of view. These questions have no answers in the Daltonian model of an atom. A knowledge of the electronic structure and the peculiarities of electron behaviour, like the orbital description and the Pauli principle, are essential, if we are to understand such important chemical facts.

EXERCISES

4.1   (i) Calculate the number of electrons which will together weigh one gram.
        (ii) Calculate the mass of one mole of electrons.
        (iii) Calculate the charge of one mole of electrons.

4.2   How many protons and neutrons are there in the following nuclei:

$^{12}_{6}C$, $^{17}_{8}O$, $^{25}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

4.3   Write the complete symbol for
        (i) the nucleus with atomic number 56 and mass number 138
        (ii) the nucleus with atomic number 26 and mass number 55
        (iii) the nucleus with atomic number 4 and mass number 9.

4.4   One of the spectral lines of caesium has a wavelength of 456 nm. Calculate the frequency of this line.

4.5   The frequency of the strong yellow line in the spectrum of sodium is $5.09 \times 10^{14} s^{-1}$. Calculate the wavelength of this light in nanometers.

4.6   What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2? What is the colour corresponding to this wavelength?

4.7   (a) An atomic orbital has n = 3 What are the possible values of l?
        (b) An atomic orbital has $l = 3$. What are the possible values of m?

4.8 Using the *s, p, d* notations, describe the orbital with the following quantum numbers·
   (a) $n = 1, \ell = 0$
   (b) $n = 2, \ell = 0$
   (c) $n = 3, \ell = 1$
   (d) $n = 4, \ell = 2$
   (e) $n = 4, \ell = 3$

4.9 Using the Aufbau principle, write the electron configuration for the ground state of the following atoms:
   Boron ($Z=5$), Neon ($Z=10$), Al ($Z=13$), Chlorine ($Z=17$), Calcium ($Z=20$), Rubidium ($Z=37$).

4 10 (a) What is the shape of: (i) an *s* orbital (ii) a *p* orbital?
   (b) Which of the following orbitals are spherically symmetric?

      (i) p_x (ii) *s* (iii) p_y

4.11 From the following sets of quantum numbers, state which are possible. Explain why the others are not permitted.

   (i) $n = 0, \quad \ell = 0, \quad m = 0, \quad s = +\frac{1}{2}$

   (ii) $n = 1, \quad \ell = 0, \quad m = 0, \quad s = -\frac{1}{2}$

   (iii) $n = 1, \quad \ell = 1, \quad m = -0, \quad s, = +\frac{1}{2}$

   (iv) $n = 1, \quad \ell = 0, \quad m = +1, \quad s = +\frac{1}{2}$

   (v) $n = 2, \quad \ell = 1, \quad m = -1, \quad s = -\frac{1}{2}$

   (vi) $n = 2, \quad \ell = 2, \quad m = 0, \quad s = -\frac{1}{2}$

   (vii) $n = 2, \quad \ell = 1, \quad m = 0, \quad s = +\frac{1}{2}$

U N I T 5

CHEMICAL FAMILIES—PERIODIC PROPERTIES

Properties of elements are periodic functions of their atomic numbers

OBJECTIVES

In this Unit, we shall learn

* the historical development of Mendeleev's periodic table;

* the modern periodic law and the electronic configuration of atoms as the basis for periodic classification;

* the broad categories of elements (s, p, d, f blocks) and their chief characteristics;

* the periodicity in physical and chemical properties of elements.

THERE ARE MORE than one hundred chemical elements known today It would be difficult to study individually the chemistry of all the elements and their numerous compounds. The study can be simplified if we find a way to classify the elements into various SETS OR GROUPS having similar properties The PERIODIC TABLE represents a reasonably systematic and extremely useful framework for organising the vast amount of information available on the chemical behaviour of the elements into a few simple and logical patterns In this Unit, we shall study the development of Mendeleev's periodic table and see how this empirical classification follows as a logical consequence of the electronic configuration of atoms. We shall also examine some of the periodic trends in the physical and chemical properties of the elements

The question of a rational classification of elements engaged the minds of several chemists even in the nineteenth century, notably Doebereiner, Newlands, Meyer and Mendeleev. John A.R. Newlands in 1865-1866 developed his LAW OF OCTAVES. He found that when the elements were arranged in order of their increasing atomic weights, any given element was similar to the eighth element that followed it. At that time, this idea was not widely accepted.

5 1 MENDELEEV'S PERIODIC TABLE

In 1869, J.Lother Meyer, a German, and Dmitri I Mendeleev, a Russian, independently constructed tables of elements in which those with similar properties were placed together. In these tables, the elements were arranged in the order of their increasing atomic weights. An examination of these tables showed that similarities in the physical and chemical properties appear at regular intervals. Lothar Meyer used the physical properties such as atomic volume, melting point and boiling point to arrive at his table of elements. Mendeleev's system was more elaborate. He used a broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the formulae of the compounds formed by the elements Mendeleev stated the PERIODIC LAW thus: "The properties of the elements, as well as the formulae and properties of their compounds depend in a periodic manner on the atomic weight of the elements " A table of elements in which those with similar properties are placed together is called a PERIODIC TABLE

In devising his periodic table, Mendeleev realised that some of the elements did not fit in with his scheme of classification if the order of atomic weights was strictly followed. He ignored the order of atomic weights to group together elements which had similar chemical properties. He also had the courage and foresight to leave gaps in the table for elements which were not known at that time. He could predict the properties of those missing elements from a study of the properties of other elements in the same group. For example, both gallium and germanium were not discovered at the time when Mendeleev proposed his periodic table. Mendeleev named these elements as EKAALUMINIUM and EKASILICON because he believed that they would be

similar to aluminium and silicon respectively. These elements were discovered later and Mendeleev's predictions proved remarkably correct. The properties of ekasilicon predicted by Mendeleev and found by Winkler for germanium are shown in Table 5 1

TABLE 5.1

Mendeleev's Predictions for the Element Ekasilicon (Germanium)

Property	Tin and its compounds	Silicon and its compounds	Mendeleev's predictions for ekasilicon (1871)	Winkler's report of germanium (1886)
Atomic mass	118.7	28.1	72	72.6
Density (g cm^{-3})	7 31	2.42	5.5	5.36
Melting point (K)	505 ·	1683	high	1231
Preparation of the element	Reduction of SnO_2 with carbon	Reduction of K_2SiF_6 with sodium	Reduction of MO_2 or $K_2M_2F_6$ with Na	Reduction of $K_2 GeF_6$ with Na,
Action of acid and alkali	Slow attack by Conc HCl; attacked by HNO_3, not attacked by sodium hydroxide.	Acid resistant, slow attack by alkali.	Will be slightly attacked by acid; will not be attacked by akali	Not attacked by HCl or dilute NaOH, reacts with hot Conc. HNO_3
Oxide, formula and density (g.cm^{-3})	SnO_2,7.0	SiO_2,2.65	MO_2,4.7	GeO_2,4,7
Sulphide,formula and properties.	SnS_2, insoluble in water, soluble in ammonium sulphide.	SiS_2, decomposes in water.	MS_2, insoluble in water; soluble in ammonium sulphide	GeS_2 insoluble in water and dilute acid; soluble in ammonium sulphide
Chloride formula	$SnCl_4$	$SiCl_4$	MCl_4	$GeCl_4$
Boiling point ($^-$K)	387	330.6	373	356
Density (g cm^{-3})	2 23	1.50	1.9	1.88

Because of his systematic work and far-reaching ideas, Mendeleev is usually given the credit for the design of the periodic table as we know it today. The modern periodic table is essentially similar to that of Mendeleev with a separate column added for noble gases which were not discovered until the closing years of the nineteenth century Thus the intuition of Mendeleev and the painstaking experimental work of several chemists before him culminated in the formulation of rational (though empirical) classification of the elements. Several decades had to pass before the electron 'was discovered and the modern theory of atomic structure developed (Unit 4) . Later in this Unit, we shall see how the electronic configuration of atoms provides a fundamental basis for the periodic classification of the elements.

DMITRI MENDELEEV (1834 -1907)

Dmitri Mendeleev, the youngest of a family of seventeen, was born in Tobalsk, Siberia, in Russia, After his father's death, the family moved to St. Petersburg (now called Leningrad). He obtained a Master's degree in Chemistry in the year 1856. He then taught at the University of St. Petersburg where he was appointed professor of inorganic chemistry in 1867. The necessary preliminaries for his great textbook *Principles of Chemistry* led Mendeleev to the systematic and perodic arrangement of the elements. It was a very imaginative idea to consider that the properties of the elements were in some respect related to their atomic masses, since the structure of atoms was unknown at that time. To bring certain elements into the correct group from the point of view of their chemical properties, he reversed the order of some pairs of elements and asserted that their atomic masses were incorrect. When the periodic table was set up, many vacant spaces became evident. Mendeleev was faced with the choice between abandoning his scheme as invalid or declaring that these vacant spaces must belong to undiscovered elements. He chose the latter alternative and boldly predicted the properties of some of these unknown elements from the trends that he observed among the properties of related elements.
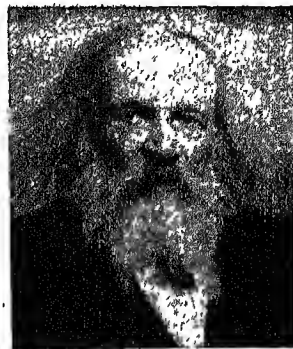
The success of Mendeleev's approach was especially evident with regard to the three elements that he called eka-boron, eka-silicon, eka-aluminium. They were subsequently given the names scandium, germanium and gallium by their discoverers. The properties of the three elements were found to be astonishingly close to Mendeleev's predictions.

Mendeleev was a versatile genius who was interested in many fields of science. He worked on many problems associated with Russia's natural resources. He invented an accurate barometer. In 1890 Mendeleev resigned

from his professorship. He was then appointed Director of the Bureau of Weights and Measures, where he continued to carry out important researches until his death in 1907.

5.2   MODERN PERIODIC LAW

As we have already stated, Mendeleev's periodic classification of elements is based on their atomic masses. We now recognise that atomic number is a more fundamental property than atomic mass. A modern version of the periodic law may be stated as follows: "The physical and chemical properties of the elements are the periodic functions of their atomic numbers." You may recall that the atomic number is equal to the nuclear charge or the number of electrons in an atom. The periodic table thus classifies elements based on their electronic configurations which indeed determine the physical and chemical properties of the elements and their compounds.

There are many forms of the periodic table. The long form shown in Fig. 5.1 is the most convenient and the most widely used. The horizontal rows are called PERIODS. Elements having similar chemical and physical properties appear in vertical columns and are referred to as GROUPS or FAMILIES. There are altogether seven periods. The first period contains 2 elements. The subsequent periods consist of 8, 8 18, 18 and 32 elements. The seventh period is incomplete and like the sixth period would have a theoretical maximum of 32 elements.

There is a close connection between the electronic configuration of the elements and the long form of the periodic table. We have already learnt that an electron in an atom is characterised by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the SHELL. Each successive period in the periodic table is associated with the filling up of the next higher principal energy level (n=1, n=2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period has thus the two elements— hydrogen ($1s^1$) and helium ($1s^2$) and the first shell (K) is completed. The second period starts with lithium in which one electron enters the $2s$ orbital. The L shell is complete at neon ($2s^2\ 2p^6$) and there are 8 elements in the second period. The third period (n=3) begins at sodium, the least tightly bound electron entering a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period (n=4) starts at potassium with the filling up of $4s$ orbital. Now you may note that before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and we come across the so called $3d$ TRANSITION SERIES of elements. The fourth period ends at krypton with the filling up of the $4p$ orbitals.

Representative elements

d—transition elements

Representative elements

Noble gases

Long form of the Periodic Table of the Elements

Main table (GROUP NUMBER 1–18, PERIOD NUMBER 1–7):

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^1 7s^2$	104 Unq	105 Unp	106 Unh	107 Uns											

f—inner transition elements

*Lanthanides $4f^n 5d^{0-1} 6s^2$

58 Ce $4f^1 5d^1 6s^2$	59 Pr $4f^3 5d^0 6s^2$	60 Nd $4f^4 5d^0 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$

**Actinides $5f^n 6d^{0-1} 7s^2$

90 Th $5f^0 6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 6d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^0 7s^2$

Fig. 5.1 Long form of the Periodic Table of the Elements with their atomic number and ground state electronic configurations. The groups are numbered 1—18 in accord with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA—VIIA, v, IB—VIIB and VIII for s, p, and d, block elements.

Altogether we have 18 elements in the fourth period. The fifth period (n=5) beginning with rubidium is similar to the fourth period and contains the second d transition series starting at yttrium(Z=39). This period ends at xenon with the filling up of the 5p orbitals. The sixth period (n=6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in that order. Filling up of the 4f orbitals begins with cerium (Z=58) and ends at lutetium (Z=71) to give the first f transition series which is called the LANTHANIDE SERIES. The seventh period (n=7) would have been similar to the sixth period with the filling up of the 7s, 5f, 6d and 7p orbitals. This series is however incomplete. It includes most of the man-made radioactive elements. Filling up of the 5f orbitals after actinium (Z=89) gives the second f transition series known as the ACTINIDE SERIES The 4f and 5f transition series of elements are placed separately in the periodic table to save space and to keep elements with similar properties in a single column.

5.3 TYPES OF ELEMENTS

The atoms of the elements in a single vertical column have the same or very similar electronic configurations in the highest occupied orbitals and are therefore said to belong to the same GROUP or FAMILY of elements. According to the new recommendation of the International Union of Pure and Applied Chemistry, the groups are numbered from 1 to 18 Based on the electronic configuration, we can classify elements into four types as marked in the periodic table (Fig. 5.1).

5 3 1 Noble Gases

The noble gases are found at the end of each period in group 18. With the exception of helium these elements have ns^2 np^6 electronic configuration in the outermost shell. Helium has 1s configuration An the energy levels that are occupied by the electrons are completely filled and this stable arrangement of electrons cannot be easily altered by the addition or removal of electrons. These elements exhibit very low chemical reactivity

5 3.2 Representative Elements (s and p-block) Elements

The elements of group 1 (alkali metals), group 2 (alkaline earth metals) and groups 13 to 17 constitute the representative elements. The outermost electronic configuration changes from ns^1 to ns^2 np^5. All occupied energy levels underlying the outermost shell have their full complement of electrons. It is also customary to speak of groups 1 and 2 with ns^1 and ns^2 configurations as s-BLOCK elements and groups 13-17 as p-BLOCK elements. Noble gases are also grouped with representative p-block elements as they come at the end of each horizontal series (period) of the representative elements. The chemistry of the representative elements is determined by the number of electrons in the outermost shell called the VALENCE SHELL. The number

of VALENCE ELECTRONS for groups 1 and 2 is the same as the group number; for groups 13-17, this number is obtained by subtracting 10 from the group number. Across each period the elements progressively change from metallic to non-metallic behaviour.

5 3 3   Transition Elements (d-block Elements)

These are the elements of groups 3 to 12 in the centre of the periodic table. These elements are characterised by the filling of an inner d level by electrons and are therefore referred to as d-BLOCK ELEMENTS. These elements have the outer electronic configuration $(n-1)d^{1-10}ns^{1-2}$. They are all metals. They form coloured ions and exhibit variable valency.

5 3.4   The Inner Transition Elements (f-block Elements)

The two rows of elements at the bottom of the periodic table, called the LANTHANIDE and ACTINIDE series, are characterised by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. The last electron added to each element is an f-electron. These two series of elements are hence called f-block elements. They are all metals. Within each series, the properties of the elements are quite similar.

5.4   PERIODIC TRENDS IN PROPERTIES

From the above description of the basis of the periodic classification, it follows that there is a regular periodic repetition of the electronic configuration of the elements as the charge on the nucleus increases. Regular variations in the chemical properties of the elements were observed much before periodic trends in physical properties were noticed. We shall discuss some of these trends in this section.

5 4 1   Ionisation Energy

The chemical nature of an element depends on the ability of its atoms to accept or donate electrons. A quantitative measure of these tendencies is the IONISATION ENERGY or the ELECTRON AFFINITY. The ionisation energy (IE) is defined as the energy required to remove an electron from an isolated gaseous atom (M) in its ground state

$$M\,(g) + IE \rightarrow M^+\,(g) + e^-$$
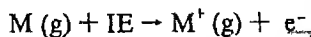
The ionisation energy is expressed in units of kJ mol^{-1}. If a second electron is to be removed from the same element the energy required will be higher than that required for the removal of the first electron because it is more difficult to remove an electron from a positively charged species than from a neutral atom. Similarly the third ionisation energy will be higher than the second and so on. If the term 'ionisation energy' is not qualified, it is taken as the *first ionisation energy*

Fig. 5 2 shows the first ionisation energies of elements up to atomic number 60. It can be readily seen that the ionisation energy of an element strongly depends on its electronic configuration and thus shows periodic variations. The maxima are found at the noble gases which have closed electron shells The high ionisation energies of the noble gases can be correlated with their extremely low chemical reactivity Similarly, the high reactivity of alkali metals is reflected in their low ionisation energies.
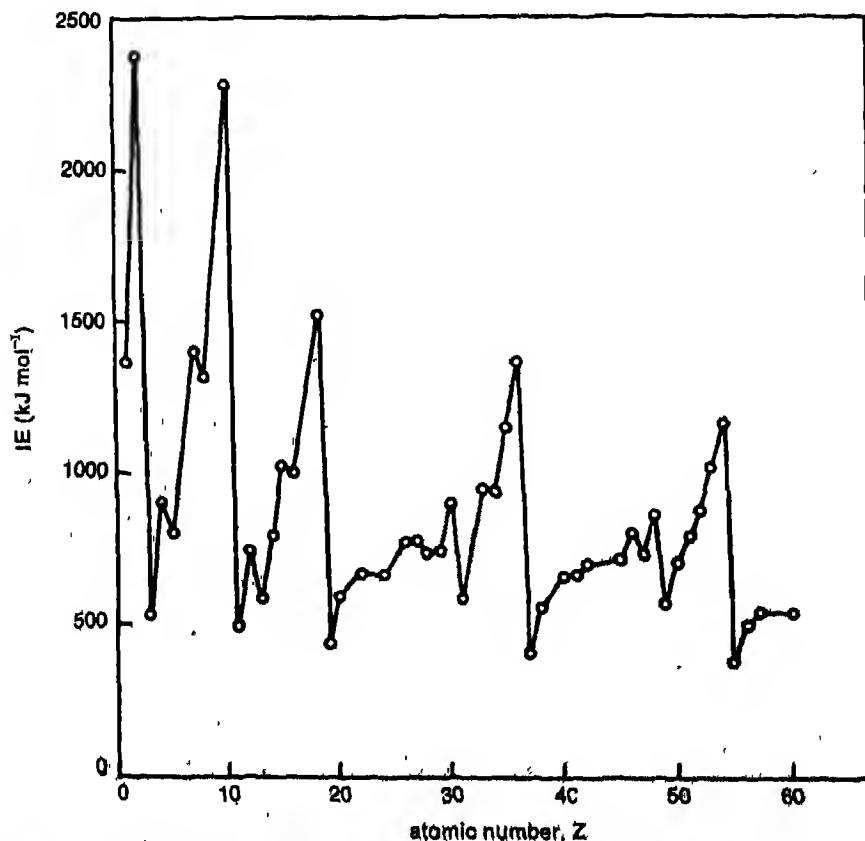
Fig. 5.2 *Variation of first ionisation energies with atomic number for elements with Z = 1 — 60*

The variations in ionisation energy across a period is illustrated in Fig. 5.3 (a) for the elements of the second period Although there are irregularities, the ionisation energy increases, from lithium to neon. This trend can be explained by considering the screening of the nuclear charge by the inner shell of electrons present between a given electron and the nucleus. The nuclear charge increases from +3 to +10 as we

go from lithium to neon. Since successive electrons are placed in the same shell, the increase in the screening of the nuclear charge by the inner 1*s* electrons is only slight and the increased nuclear charge causes the ionisation energy to increase across the period.
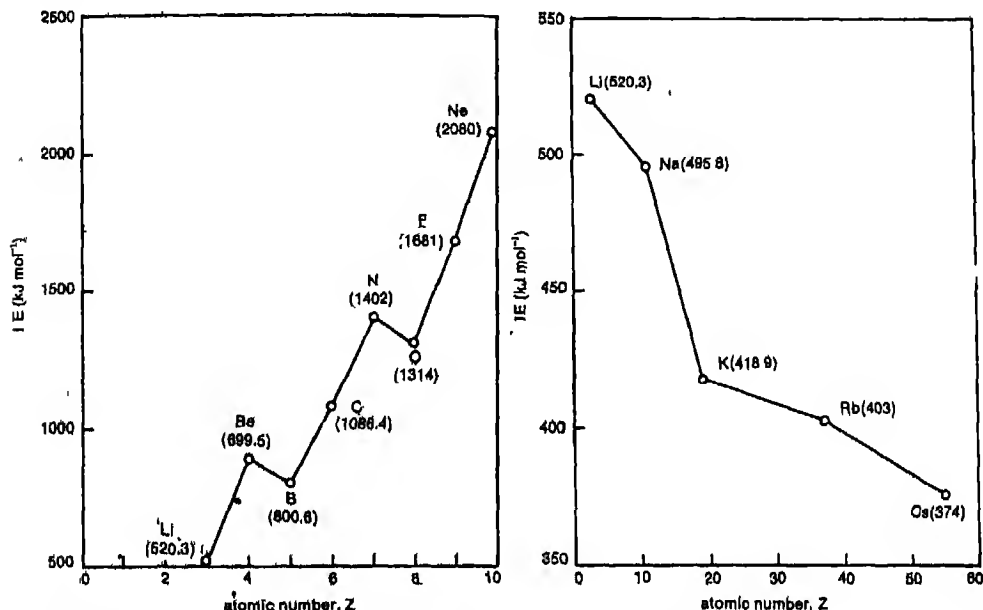
Fig. 5.3 (a) *First ionisation energies of elements of the second period as a function of the atomic number* (b) *First ionisation energies of alkali metals as a function of the atomic number*

The trend of ionisation energy within a group is shown in Fig. 5 3 (b) which gives the values for alkali metals. Generally the ionisation energy decreases as we descend the column of a group. As we go down the group, the outer electron being removed is farther from the nucleus and there is an increasing *screening* of the nuclear charge by the electrons in the inner shells. Consequently the removal of the outer electron becomes easier down a group.

5.4.2 Electron Affinity

When an electron is added to neutral gaseous atom (A) to convert it into a negative ion, the energy change accompanying the process is defined as the ELECTRON AFFINITY This can be represented by the equation:

$$A (g) + e^- \rightarrow A^- (g) + E. A.$$
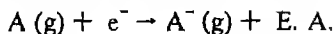
Electron affinities can be positive or negative. When energy is released in the process

of attachment of an electron to an atom, the electron affinity is taken as positive. This is the case for elements of Group 17 (halogens). These elements have high electron affinities because they can attain stable noble gas electronic configuration by picking up an electron. Electron affinity values for the halogens are shown in Fig. 5 4. Generally electron affinity decreases as we go down a group because the size of the atom increases and the electron added goes to the higher shells. It may be noted that the electron affinity of flourine does not fall in line with the general trend In this case, the effect of small size is more than offset by the repulsion of the electrons already present
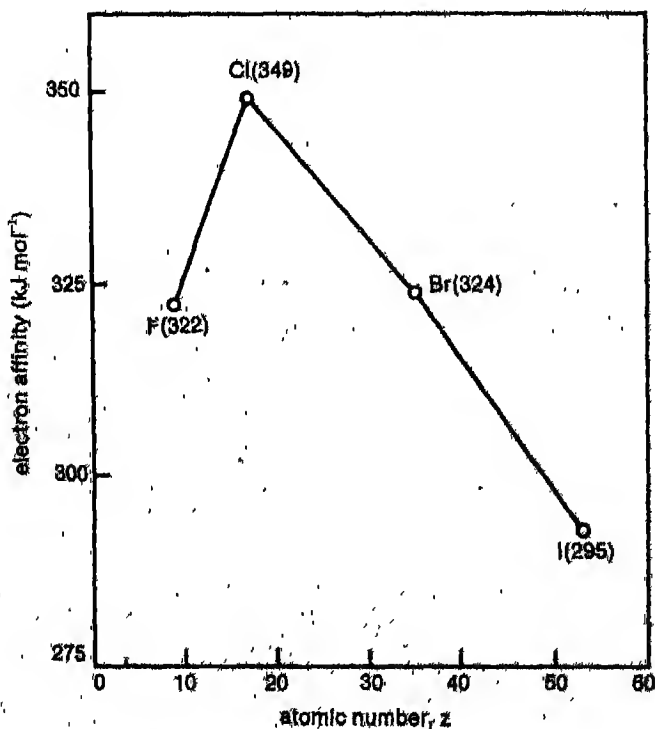
Fig. 5.4. *Electron affinities of the halogens*

Electron affinity in general increases with atomic number across a period paralleling a decrease in atomic size (Section 5.4.3). It will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus

5 4 3   Atomic Radii

It is difficult to determine the exact size of an atom or its ion An estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. For non-metallic atoms the term ATOMIC RADIUS is usually used to specify the radius of the atom bound by single covalent bond. For example, the bond distance in the hydrogen molecule (H_2) is 74 pm and half of this distance (37 pm) is taken as the atomic radius of hydrogen. For metals, atomic radius is taken as half the internuclear distance separating the metal ions in the metallic crystal The data given in Fig. 5.5 show that the atomic radius generally increases from the
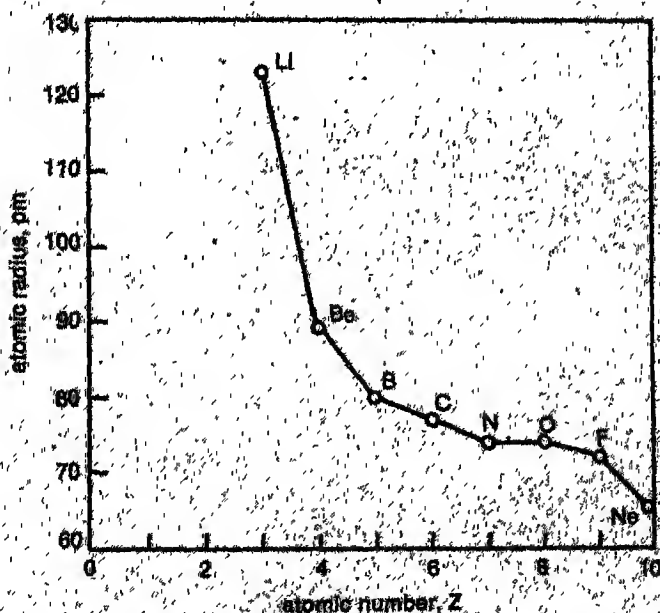
Fig. 5.5   (a) Variation of atomic radius with atomic number across the second period

top to the bottom of the periodic table and decreases on going from left to righ across the periodic table. As the nuclear charge increases, the electrons are attracted to a greater extent and atomic size decreases. Although nuclear charge increases as w go down a group, its effect is offset by the presence of a new shell of electrons and hence the atomic radius increases.

5.4.4   Valence

An important chemical property of the elements exhibiting periodic trends is thei VALENCE. Mendeleev used the formulae of the compounds formed by the element
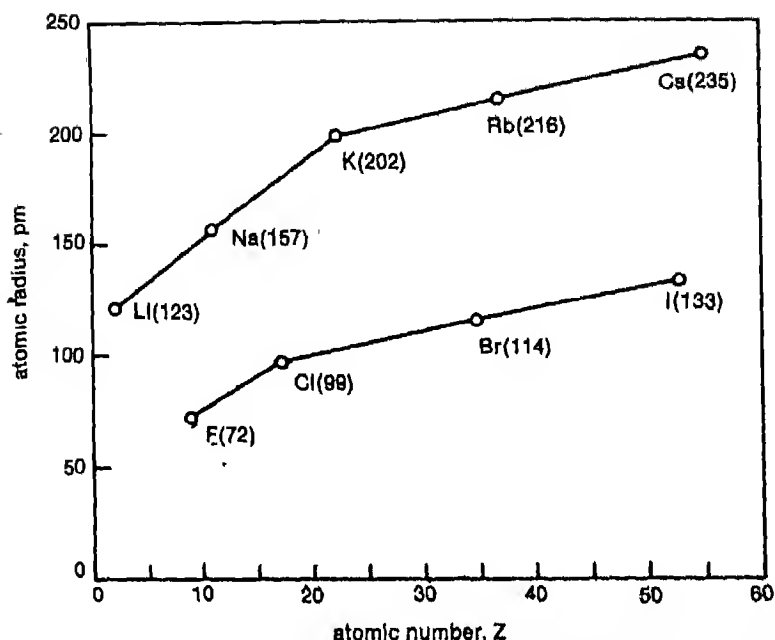
Fig. 5.5 (b) *Variation of atomic radius with atomic number for alkali metals and halogens*

as a basis for defining the groups in the periodic table that he designed. Valence can be defined in a number of ways. The formulae of compounds formed by an element are clearly linked to its valence. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of outermost electrons. Some examples are shown in Table 5.2. There are some exceptions to this rule but we shall not worry about them now.

TABLE 5.2

Periodic Trends in Valency of Elements as Reflected in the Fromulae of their Compounds

Group	1	2	13	14	15	16	17
Compounds formulae							
	HCl	BeCl$_2$	BCl$_3$	CH$_4$	NH$_3$	H$_2$O	HF
	H$_2$O	CaCl$_2$	Al$_2$O$_3$	CO$_2$	N$_2$O$_5$	H$_2$S	HCl
	LiCl	CaO	AlCl$_3$	SiO$_2$	PCl$_3$	SF$_6$	Cl$_2$O$_7$
	Li$_2$O	SrO	InCl$_3$	SnO$_2$	PCl$_5$	CS$_2$	NaBr
	NaCl	BaO	TlCl$_3$	PbO$_2$	SbCl$_3$	H$_2$Se	KI

5.4.5 Properties of Halides, Hydroxides, Sulphates of Alkali and Alkaline Earth Metals

Periodic variations are also observed in the properties of many compounds within a group of the periodic table. We shall illustrate these trends by few examples If we consider the melting points of halides of alkali metals, they decrease in the order fluoride > chloride > bromide > iodide The melting points of lithium halides are less than those of sodium halides and thereafter they decrease (with one or two exceptions) as we go from sodium down to caesium Fig. 5.6 illustrates the trends in the melting points of the chlorides of the alkali metals and also those of the sodium halides M X (X = F, Cl, Br or I).
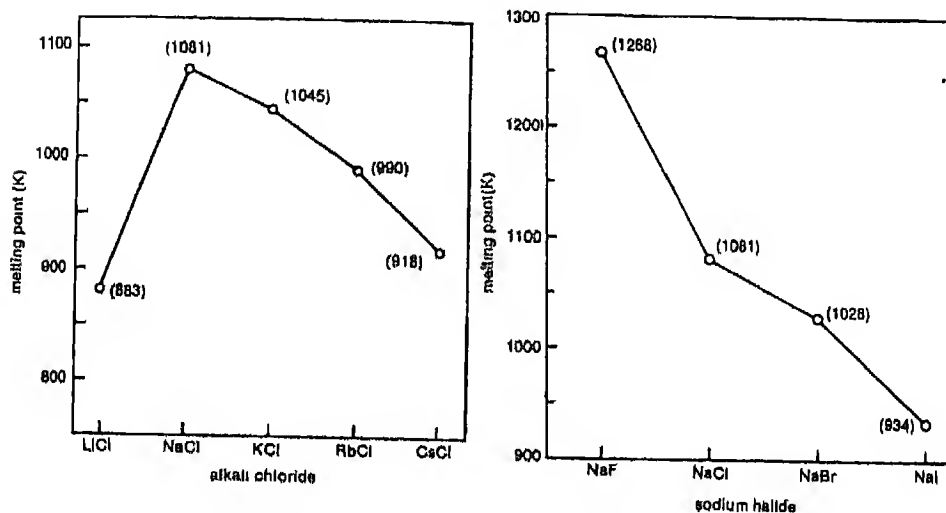
Fig. 5.6 (a) *Melting points of alkali metal chlorides* (b) *Melting points of sodium halides*

Let us now consider the solubilities of alkali metal carbonates and hydrogen carbonates in water at 298 K. The solubility increases as we go down the group from lithium to caesium as shown in Table 5.3.

There is a smooth variation in the properties of alkaline earth metal hydroxides. Their basicity and solubility in water increase as we go down the group. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong bases and barium hydroxide is nearly as strongly basic as the alkali metal hydroxides. The solubilities of hydroxides of Mg, Ca, Sr and Ba are shown in Fig. 5.7 In

TABLE5 3

Solubilities of Alkali Metal hydrogen carbonates (MHCO₃) and carbonates (M₂CO₃) in Water at 298 K.

Alkali metal	Solubility, wt %	
	$MHCO_3$	M_2CO_3
Li	5[a]	1.3
Na	9.4	22.5
K	26.6	52 9
Rb	53 7[b]	70
Cs	67 8[b]	74

a at 286 K, *b* at 293 K

contrast to the hydroxides, the solubilities of sulphates of alkaline earth metals decrease as we go down the group. Magnesium sulphate is soluble in water, $CaSO_4$ is slightly soluble and $SrSO_4$ and $BaSO_4$ are insoluble (you may recall the test for Ba^{2+} ion in qualitative analysis).
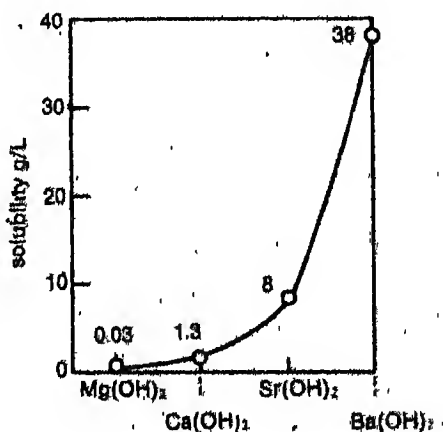
Fig. 5.7 *The solubilities of hydroxides of alkaline earth metals in water at 298 K.*

EXERCISES

5 1   What property did Mendeleev use to classify the elements in his periodic table?

5 2   State the modern 'Periodic Law'.

5 3   Explain the terms 'ionisation energy' and ' electron affinity'.

5.4   Among the elements Li, K, Ca, S and Kr which one has the lowest first ionisation energy? Which has the highest first ionisation energy?

5.5   Among the elements of the second period Li to Ne pick out the element
      (i) with the highest first ionisation energy,
      (ii) with the highest electronegativity;
      (iii) with the largest atomic radius,
      (iv) that is the most reactive non-metal,
      (v) that is the most reactive metal.

5 6   Which of the following pairs of elements would you expect to have lower first ionisation energy? Explain.
      (i) Cl or F (ii) Cl or S (iii) K or Ar (iv) Kr or Xe

5.7   Why does the first ionisation energy increase as we go from left to right through a given period of the periodic table?

5.8   Which of the following pairs of elements would have a higher electron affinity?
      (i) N or O (ii) F or Cl. Explain.

5 9   Predict the density of Cs from the density of the following elements.
      K 0.86 g cm^3,   Ca 1.548 g/cm^3,   Sc 2.991 g/cm^3
      Rb 1.532 g cm^3 Sr 2.68 g/cm^3 Y 4.34 g/cm^3
      Cs ?   Ba 3.51 g cm^3, La 6.16 g/cm^3

5 10   Account for the fact that the 4th period has eighteen and not eight elements.

5 11   Give the formula of a species that will be isoelectronic with the following atoms or ions
      (i) Ne (ii) Cl (iii) Ca^{++} (iv) Rb$^+$

5 12   The valence of representative element is either equal to the number of the valence electrons or eight minus this number. What is the basis of this rule?

5.13   How do atomic sizes vary in a group and in a period? Give reasons for the variations.

5.14   Which of the following pairs would have a larger size? Explain.
      (i) K or K$^+$ (ii) Br or Br (iii) O^2 or F
      (iv) Li$^+$ or Na$^+$ (v) P or As (vi) Na$^+$ or Mg^{2+}

5.15   Lanthanides and actinides are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.

5.16   The elements, Z = 107 and Z = 109 have been made recently; element Z = 108 has not yet been made. Indicate the groups in which you will place the above elements.

5.17   Give the characteristic properties of s, p, d and f-block elements.

5.18   The first (IE$_1$) and the second (IE$_2$) ionisation energies (kJ/mol) of a few elements designated by Roman numerals are shown below

	IE$_1$	IE$_2$
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above elements is likely to be:

   (i) a reactive metal;
   (ii) a reactive non-metal,
   (iii) a noble gas;
   (iv) a metal that forms a stable binary halide of the formula, AX_2 (X = halogen).

BONDING AND MOLECULAR STRUCTURE

Have pair—will share

OBJECTIVES

In this Unit, we shall learn

* the explanation of the following:
Octet rule; ionic bond, covalent bond, coordinate covalent bond, hydrogen bond; single bond, double bond, triple bond; polar molecules;

* to write the Lewis structures of simple molecules;

* the shapes of simple molecules using the (i) valence shell electron pair repulsion theory, and (ii) orbital overlap model.

WE HAVE LEARNT EARLIER that a group of atoms having characteristic properties is known as a molecule. Without considering their electronic structure, it is possible to obtain some information about the nature of molecules. For example, the relative numbers of different kinds of atoms (empirical formula), the actual number of different atoms (molecular formula), and even the relative arrangement of atoms (structural formula) in molecule can be obtained from chemical analysis and chemical behaviour. However, a number of interesting and important aspects of molecules can only be understood by considering their electronic structure. Let us consider the example of the hydrogen molecule which contains two hydrogen atoms. We would like to know what holds the two atoms together in this molecule. We would also like to know why molecules like H_3, H_4, H_5, etc, do not exist. Molecules have characteristic shapes. For example, the water molecule (H_2O) is angular, methane (CH_4) is tetrahedral and so on. Molecular shapes have a profound influence on physical and chemical behaviour. Had H_2O been a linear molecule instead of being a bent one, it would have had a different set of properties from those we are used to. Obviously, it is important to understand the factors responsible for the shapes and geometries of molecules.

6.1   CHEMICAL BONDS AND LEWIS STRUCTURE

Let us begin by considering the important question of how atoms are held together in compounds like NaCl and Cl_2. We say that a chemical bond exists between the atoms whenever they are strongly held together as in a molecule. In other words, the term 'chemical bond' expresses the existence of strong forces of attraction between the atoms. From the point of view of behaviour a group of atoms held together has very different properties from the isolated atoms. Thus, two H atoms and one O atom have very different physical and chemical properties compared to the molecule H_2O held together by chemical bonds, i.e., attractive forces.

The attractive force responsible for molecule formation is the electrical force between electrons and nuclei. However, not all electrons in an atom are involved in molecule formation. The inner shell electrons are well protected and they are, therefore, generally not involved in the combination process. In discussing chemical bonds, it is adequate to consider only the outer shell electrons also called the valence electrons. The great American chemist, Gilbert Newton Lewis, introduced simple symbols to denote the valence shell electrons in an atom. These symbols, called ELECTRON DOT SYMBOLS or LEWIS SYMBOLS, do not show inner shell electrons; the outer shell electrons are shown as dots surrounding the symbol of the element. Some examples of Lewis symbols are:

These symbols contain a lot of information. The number of electron dots indicates the number of outer shell (or valence) electrons. For Li, Be, B and C, this number also indicates the common valence of the element Thus, lithium is monovalent, beryllium is divalent, boron is trivalent and carbon is tetravalent. However, the common valence of nitrogen, oxygen, fluorine and neon is 3,2,1 and 0 respectively This means that the valence of these elements can be obtained from the Lewis symbols by *subtracting* the number of dots from 8 To summarise, the common valence of an element is *either* equal to the number of dots in the Lewis symbol *or* it is equal to 8 minus the number of dots.

Octet Rule: It is a fact that both neon and argon are not known to form any compounds and both the elements are monatomic. It is also a fact that a neon atom as well as an argon atom have eight electrons in their valence shell. These observations suggest that a valence shell containing eight electrons is particularly stable. Lewis therefore put forward the so-called Octet Rule according to which an atom tends to gain, lose or share electrons during molecule formation, such that there are eight electrons surrounding it. The Octet Rule is very useful to explain the normal valences of the elements in a wide variety of situations.

Gain and Loss of Electrons (Ionic Bond) The most obvious way for an atom to have an octet in its valence shell is to acquire additional electrons if it has less than eight valence electrons or to lose all its outer electrons. For example, a chlorine atom has the electron configuration 2,8,7. It can have eight electrons (i e , an octet) in the third shell by gaining one electron. On the other hand, a sodium atom with the configuration 2,8,1 can have the octet in the second shell if it can lose an electron. We can now understand the reaction between sodium and chlorine to form sodium chloride Each sodium atom loses one electron to form a sodium ion Na^+ , while each chlorine atom acquires an electron to form chloride ion, Cl^- . In terms of the Lewis structure, the reaction is written as

$$Na + Cl \rightarrow (Na^+) \ (Cl^-)$$
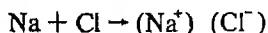
The formation of opposite charges leads to an attractive force between the sodium and chloride ions. Solid sodium chloride (NaCl) consists of an array of Na^+ ions and Cl^- ions held together by electrostatic attraction. Such an electrostatic force between oppositely charged ions is called an IONIC BOND

The formula of solid sodium chloride can be written as NaCl or Na^+Cl^- (see Unit 3). It should be realised that this represents the empirical formula. The question of assigning a molecular formula does not arise as a solid ionic compound does not contain any molecule. The empirical formula of an ionic compound is easily derived if the valence of the elements forming the compound is known The valence is equal to either the number of electrons lost to form the positive ion or to

the number of electrons gained to form the negative ion. In short, the valence is equal to the charge on the ion.

Listed below are the common monatomic ions of the main group elements.

1	2	13	14	15	16	17
Li^+	Be^{2+}			N^{3-}	O^{2-}	F^-
Na^+	Mg^{2+}	Al^{3+}		P^{3-}	S^{2-}	Cl^-
K^+	Ca^{2+}					
Rb^+	Sr^{2+}					Br^-
Cs^+	Ba^{2+}					I^-

Example 6.1

Give the empirical formulas and Lewis structures for the ionic compound formed by each of the following pairs of elements:
K, O; Ca, Cl, Na, S; Al, F; Na, P.

Solution

From the charges on the ions, the ratio of the numbers of positive and negative ions in the compound can be found out. This gives the empirical formula. The Lewis structure is then easily written.

Ions	*Formula*	*Lewis Structure*
K^+, O^{2-}	K_2O	$(K^+)_2 (:\ddot{O}:^{2-})$
Ca^{2+}, Cl^-	$CaCl_2$	$(Ca^{2+}) (:\ddot{Cl})_2$
Na^+, S^{2-}	Na_2S	$(Na^+)_2 (.\ddot{S}:^{2-})$
Al^{3+}, F^-	AlF_3	$(Al^-) (F.)_3$
Na^+, P^{3-}	Na_3P	$(Na^+)_3 (:P.^{3-})$

Sharing of Electrons (Covalent Bond): The loss or gain of electrons so that a stable octet results, explains the formation of many ionic compounds. In all such cases, dissimilar atoms are involved. However, there are a large number of instances e.g. Cl_2, where the atoms involved are similar. Obviously, gain and loss of electrons cannot be involved in such cases. Lewis therefore suggested that in a molecule like Cl_2, the octet is completed by *sharing* a pair of electrons.

$$:\ddot{Cl} + \cdot\ddot{Cl} \longrightarrow :\ddot{Cl}:\ddot{Cl}:$$
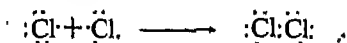
As can be seen, the shared pair helps both the atoms to have eight electrons in their valence shells. Consider another example, PCl_3. The phosphorus atom has five valence electrons. It can acquire three electrons from three chlorine atoms.

$$\cdot \ddot{P} \cdot + 3 \cdot \ddot{Cl} \colon \; \rightarrow \; \cdot \ddot{Cl} \; \ddot{P} \colon \ddot{Cl} \colon$$
$$\colon \ddot{Cl} \colon$$
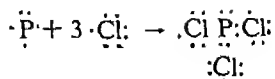
Once again, sharing enables each atom to have the octet

Whenever two atoms are held by a pair of shared electrons, a COVALENT BOND is said to exist between them. The Cl_2 molecule has one covalent bond while the PCl_3 has three covalent bonds To simplify writing, a covalent bond is shown as a line between the two atoms. Thus, Cl_2 and PCl_3 are written as

$$\colon \ddot{Cl} - \ddot{Cl} \cdot \qquad\qquad \colon \ddot{Cl} - \ddot{P} - \ddot{Cl} \cdot$$
$$\colon \ddot{Cl} \colon$$

In the above formulas, the valence electrons *not* involved in bonding (i.e., sharing) have been shown explicitly Such electrons are called NONBONDING PAIRS, LONE PAIRS, or UNSHARED PAIRS. Each chlorine atom in both the examples has three lone pairs. The phosphorus atom in PCl_3 has one unshared pair. When bonds are shown as lines, it is a common practice not to write all the lone pair electrons explicitly. Thus, Cl_2 and PCl_3 are usually written as

$$Cl - Cl \quad , \quad Cl - P - Cl$$
$$Cl$$
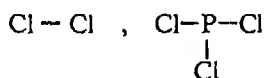
Multiple Bonds: Consider the molecule CO_2. Since a carbon atom has four valence electrons and an oxygen atom has six, it is not possible to write any Lewis structure in which only *one* electron pair is shared. However, by sharing two electron pairs, it is possible to obey the octet rule.

$$\colon \ddot{O} \colon\colon C \colon\colon \ddot{O} \colon$$
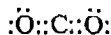
Two shared pairs of electrons are shown by two lines.

$$\colon \ddot{O} = C = \dot{O} \cdot$$

Such a bond is called a DOUBLE BOND. Extension of reasoning to N_2 shows that in this case the octet rule requires that three electron pairs are shared.

$$:N \quad . \ N:$$

N_2 molecule is written as

$$:N \equiv N:$$

This is an example of a TRIPLE BOND.

Example 6 2

Draw the Lewis structure for carbon tetrachloride (CCl_4), a colourless liquid and a good solvent for oils and grease

Solution

The Lewis symbol for carbon (which is in group 14 of the periodic table) is $\cdot\overset{\cdot}{C}\cdot$ It thus needs four more electrons to complete its octet. Chlorine is in group 17 of the periodic table and needs one more electron to complete the octet. The Lewis symbol for chlorine is $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$ It is obvious that four chlorine atoms can share four pairs of electrons with one carbon atom yielding complete octets for all the atoms. This can be expressed as follows.

$$\cdot\overset{\cdot}{C}\cdot + 4\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot \rightarrow :\overset{:\overset{\cdot\cdot}{Cl}:}{\underset{\cdot\overset{\cdot\cdot}{Cl}\cdot}{Cl}}:C:Cl: \quad \text{or} \quad \begin{array}{c} Cl \\ | \\ Cl -C- Cl \\ | \\ Cl \end{array}$$
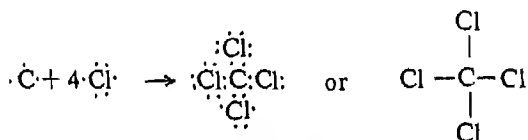
Exceptions to the Octet Rule: Although very useful in a large number of cases, the octet rule has many exceptions. Let us consider three types of exceptions.

A hydrogen atom has only one electron in the first ($n = 1$) valence shell Only one more electron is needed to fill this shell. The completed shell has the same electron arrangement as the noble gas helium. In this case, therefore, an octet is not needed to achieve a stable configuration. Lewis structure for molecules containing hydrogen is easily written if this restriction is kept in mind. The electron dot structures of a few molecules containing hydrogen atom is shown below·

$$H_2 \Rightarrow H:H, \quad H_2O \Rightarrow H:\overset{\cdot\cdot}{O}:, \quad NH_3 \Rightarrow H.\overset{\cdot\cdot}{N}.H, \\ \qquad\qquad\qquad H \qquad\qquad\qquad \overset{..}{H}$$

$$CH_4 \Rightarrow H:\overset{\overset{H}{\cdot\cdot}}{\underset{\overset{\cdot\cdot}{H}}{C}}H$$
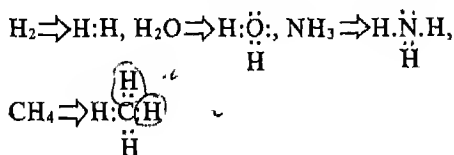
On the basis of the octet rule, elements in groups 1, 2 and 13 should not form covalent compounds. This is because they have less than four electrons in their valence shell and cannot therefore achieve an octet by electron sharing. However,

this prediction. [faded text] of these group [faded text] but the octet is incomplete (only six electrons surround the boron atom).

$$BF_3 \Rightarrow :\!\ddot{F}\!:\!\ddot{B}\!:\!\ddot{F}\!: \qquad BCl_3 \Rightarrow :\!\ddot{Cl}\!:\!\ddot{B}\!:\!\ddot{Cl}\!:$$
$$\cdot\ddot{F}\cdot \qquad\qquad\qquad :\!\ddot{Cl}\!:$$
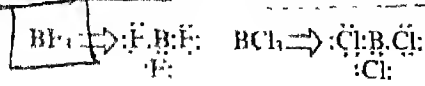
The third type of violation of the octet rule is observed for elements which have more than eight electrons in their valence shells. PF_5 and SF_6 are two such examples, where [faded text] the central atoms are surrounded by 10 and 12 electrons respectively.

6.2 SHAPES OF MOLECULES

Molecules show geometrical patterns which are varied and artistic. Long, round, flat, and spiral shapes are known. Also known are linear, triangular, square planar, pyramidal, octahedral and many other arrangements. Many physical and chemical properties are the result of the shape that a molecule has. For example, some of the unique [faded text] of the water [faded text] of H_2O, a linear arrangement of the trial [faded text] ties. Similarly, the biologically important DNA molecule partly owes its physico−chemical behaviour to its double spiral shape. Why is it that the atoms of a molecule occupy geometrically regular locations?

We have seen that ionic bonds arise due to electrostatic attraction. Since the coulomb force is non-directional (i.e., the strength of interaction between two charges depends on the distance but not on the direction), the structure of an ionic crystal is determined almost entirely by the relative sizes of the ions. Covalent bonds are, however, directional. The shape of a covalently bonded molecule is therefore [faded text] directions of the covalent bonds. [faded text] determination of molecular geometry is a fascinating field. Chemists today have a wide variety of methods which permit measurement of distances and angles between the atoms. We will not consider this aspect here but only discuss some of the basic ideas of the valence shell electron pair repulsion (VSEPR) theory which enable us to understand why molecules have characteristic shapes.

6.2.1 VSEPR Theory

According to the valence shell electron pair repulsion (VSEPR) theory the direction of the bonds around an atom in a molecule depends on the total number of electron pairs (bonding as well as non-bonding) in the valence shell of the atom. Since the electron pair repel each other strongly, that geometrical arrangement is favoured which places the electron pairs as far as possible. Let us see how this theory is

applied to the molecules of the type AB_n where A is the central atom and n is the number of B atoms that attach to A by single electron pair bonds.

Consider the molecule $BeCl_2$. Here Be is the central atom. The Lewis structure of the molecule is

$$:\ddot{C}l:Be:\ddot{C}l:$$
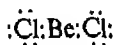
There are only two electron pairs in the valence shell of the beryllium atom. The geometry of the molecule is therefore linear since the two electron pairs are placed at 180° with respect to each other.

In the molecule BF_3 ($:\ddot{F}.B.\ddot{F}.$), the three electron pairs form an equilateral
$$:\ddot{F}:$$
triangular arrangement, BF_3 is therefore a planar molecule with $\angle FBF = 120°$. The four electron pairs in CH_4 favour a tetrahedral arrangement which explains the tetrahedral shape of methane. Other examples of tetrahedral molecules like CCl_4, SiF_4, SiH_4, NH_4^+, BF_4 also have four electron pairs in the valence shell of the central atom.

It is interesting to note that HF, H_2O and NH_3 also belong to the category of four electron pairs though in these cases some of the pairs are of the non-bonding type (HF has three non-bonding pairs, H_2O has two, and NH_3 has one). The four electron pairs occupy vertices of a tetrahedron from which the geometry of the three molecules can be deduced in the following way.

NH_3: In this case, three vertices are occupied by the hydrogen atoms and the fourth by the non-bonding pair. This geometry is such that the three hydrogen atoms form an equilateral triangle with the nitrogen atom at the apex of the triangular pyramid. Ammonia molecule has therefore a triangular pyramidal shape. Note that $\angle HNH$ is the same as in a tetrahedron, namely 109.5°. The same analysis applies to molecules like PCl_3, NF_3 and H_3O^+.

H_2O: Two corners of the tetrahedron are occupied by the hydrogen atoms and the remaining two corners by the non-bonding pairs. H_2O is thus predicted to be angular with $\angle HOH = 109.5°$. Other molecules with same shape are F_2O, NH_2^- and SCl_2.

HF: This molecule is necessarily linear since it contains only two atoms though in this case also, the four electron pairs form the tetrahedral geometry.

We have so far considered up to four electron pairs. In PCl_5, the central phosphorus atom has five electron pairs. The arrangement which keeps the five pairs as far apart as possible is trigonal bipyramid, the shape of the PCl_5 molecule. Similarly, SF_6 is octahedral because the repulsion between the six electron pairs around the central sulphur atom is minimised this way. Fig 6.1 shows the shapes of various categories of molecules.

number of pairs	2	3	4
arrangement of pairs	linear	trigonal planar	tetrahedral

number of pairs	5	6
arrangement of pairs	trigonal bipyramidal	octahedral
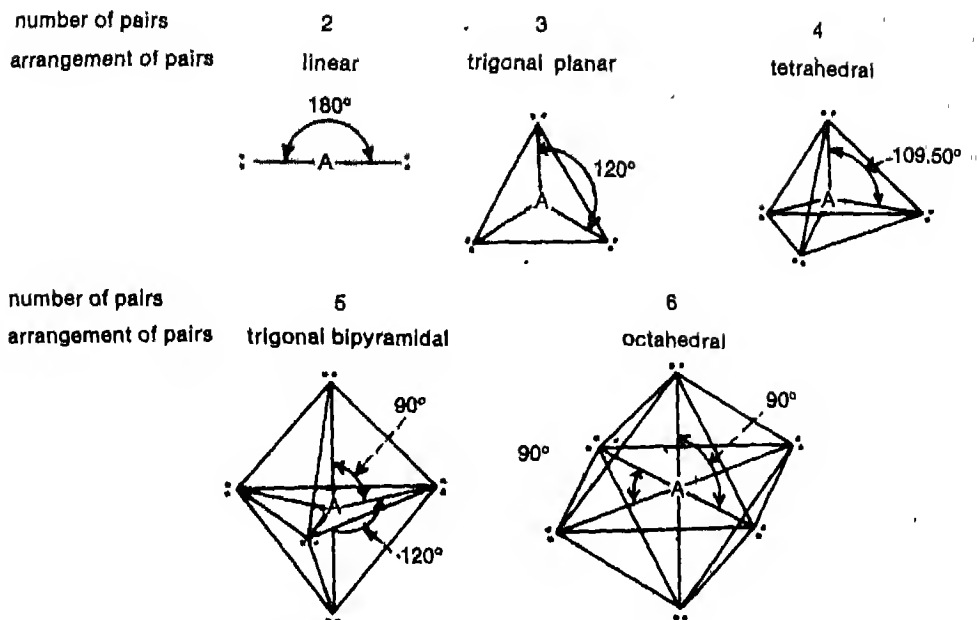
Fig. 6.1 *The various geometries based on the electron repulsion model. In each case the given arrangement minimises the electron pair repulsion.*

The molecular shapes deduced by the VSEPR theory have been verified by experiments. The theory thus provides a reliable method for understanding and predicting molecular geometry.

6.3 QUANTUM THEORY OF THE COVALENT BOND

We have so far described chemical bonding and molecular shapes in terms of electron dot structures and the electron pair repulsion theory. In the study of atomic structure, it was shown that a proper description of electron behaviour requires the use of quantum mechanical ideas which includes the orbital concept and the Pauli exclusion principle. We therefore turn now to a deeper view of the covalent bond based on the quantum theory. Just as it was convenient to discuss the electronic structure of atoms in terms of the hydrogen atom—the simplest atom—it will be convenient to begin here with the hydrogen molecule (H_2)— the simplest molecular system.

6.3.1 The Hydrogen Molecule

Experiments show that if a mole of H_2 molecules is heated to a sufficiently high temperature, the following reaction takes place:

$$H_2(g) + 433 \text{ kJ} = H(g) + H(g)$$
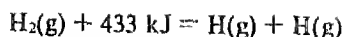
This equation tells us that a mole of H_2 molecules needs 433 kJ of energy to dissociate into hydrogen atoms Conversely, the formation of a mole of H_2 molecules from hydrogen atoms releases 433 kJ of energy. A _____ energy (i.e., it is more stable) tha _____ to an H_2 molecule It is alway· _____ . has lower energy as compared to the isolated atoms. We conclude that atoms form molecules because the latter are more stable. Energy is liberated when a molecule is formed, but energy is needed to break a molecule.

What makes a hydrogen molecule more stable than two hydrogen atoms? Consider a single hydrogen atom as in Fig. 6.2a. The electron in the $1s$ orbital, as you know, corresponds to the probability distribution having the lowest energy. This distribution is spherically symmetrical meaning that it is the same _____ The average distance of the electron from the nucleus in this orbital is 0.53 × 10 m. The average distance in other orbitals is larger

(a)

(b)

(c)

(d)
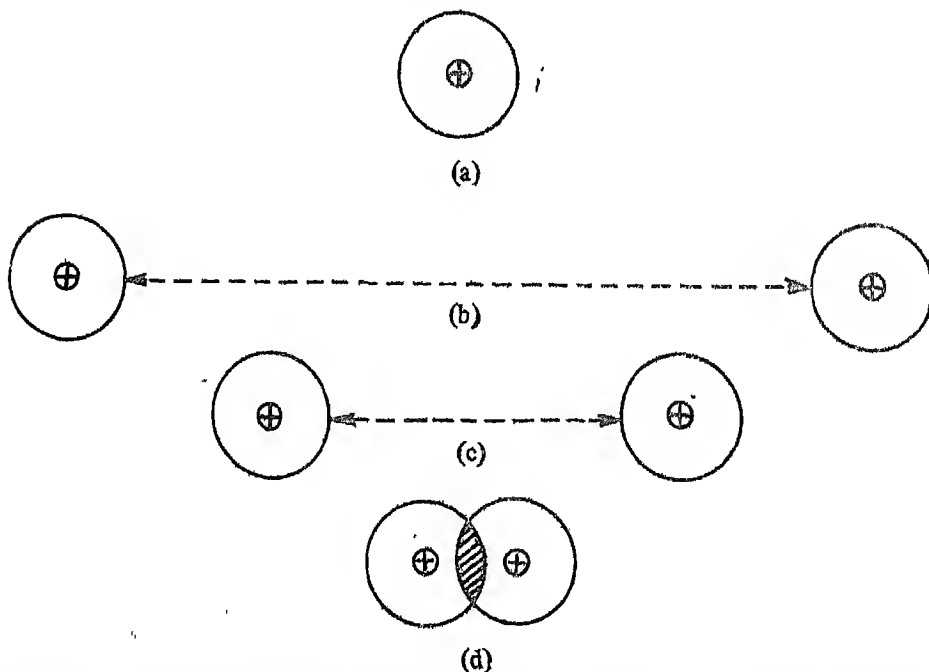
Fig. 6.2   Formation of hydrogen molecule, (a) a simple representation of the hydrogen atom (shown as in orbital), (b) two hydrogen atoms at large separation and therefore no interaction, (c) two hydrogen atoms with moderate separation-interaction starts, and (d) two hydrogen atoms as in H_2 molecule.

Imagine a second hydrogen atom (also having an electron in the $1s$ orbital) at a large distance from the first as shown in Fig. 6 2b. There is virtually no interaction between the two atoms at this distance and the total energy is just the sum of the energies of the individual atoms. Because energy is not lowered, no stability results. Molecule formation is thus not expected at large separations. The situation, however, changes if the two atoms are brought closer together as in Fig 6.2c. The electron of one atom begins to experience the attractive force of the nucleus of the other atom. As the atoms are brought still closer as in Fig. 6.2d the electron of one atom will be strongly attracted by the nucleus of the other atom. In an isolated hydrogen atom the electron is attracted by only a single nucleus, but when two hydrogen atoms are close together (Fig. 6.2d) each of the two electrons experiences the attractive pull of two nuclei. This is obviously a more favourable situation and we expect the energy to be lowered.

What about the repulsive forces between the two electrons and between the two nuclei? Certainly, these increase as the two atoms come closer. It can be shown that there exists a critical distance where the attractive and repulsive influences balance each other. At distances larger than this, the attractive force is stronger while at smaller distances, the repulsive force is more powerful (Fig. 6.3). Maximum lowering of energy takes place at this critical distance, which is equivalent to saying that a set of two hydrogen atoms has lowest energy at the critical distance. Under these conditions, the two hydrogen atoms form a stable grouping called a hydrogen molecule.
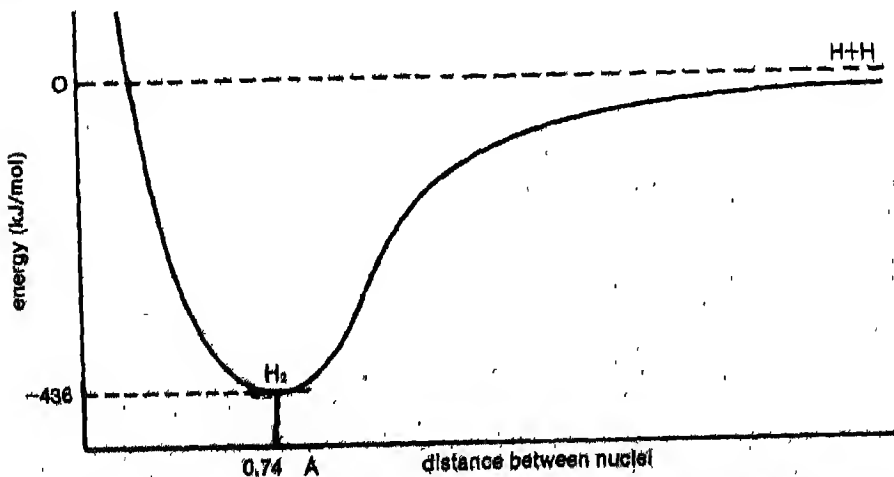
Fig. 6.3 *Energy of system of two hydrogen atoms as a function of internuclear separation. The minimum (at—436 kJ mol⁻¹) in the energy curve represents the equilibrium internuclear separation (at 0.74 Å, i.e. 0.74 × 10⁻¹⁰ m) which is known as bond length in the hydrogen molecule.*

Chemical Bond in H_2 Molecule: When the idea of a molecule was first introduced, chemists thought that the component atoms of a molecule are held together by bonds. As stated earlier, these bonds are symbolically represented by drawing a line between the atoms. Thus, H_2 molecule is written as H-H. The nature and origin of such chemical bonds cannot be understood on the basis of a structureless atom. By taking into account the attraction and repulsion of the electrons and the nuclei, we have now seen how a group of atoms acquires stability. In the case of H_2, the primary cause of stability is the attraction that each of the two electrons experiences from both the nuclei simultaneously. The two electrons are a kind of cement which hold the two nuclei together. One may say that the pair of electrons shared by the two nuclei is the chemical bond. We now see the importance of electron pairs in the Lewis structures The line drawn between two atoms to represent a chemical bond in the older formulation corresponds to a shared pair of electrons in the modern approach. Such a sharing of electron pair between two atoms is termed covalent bond. The electron pair may be shared equally by the two atoms as in the case of the hydrogen molecule where the two atoms are identical. In cases where the two atoms are not identical the sharing may not be equal.

The ⋯⋯⋯⋯⋯ ce corresponding to the minimum energy and maximum ⋯⋯⋯⋯⋯⋯ bond length. Experiments have shown that the bond length (distance between the two hydrogen nuclei) in an H_2 molecule is 0.74×10^{-10}m. The energy corresponding to this minimum is called the bond energy. If this much energy is supplied from outside, the bond will break and the molecule will dissociate. Dissociation energy is equal to bond energy for a molecule containing one bond only. The dissociation energy per mole of H_2 molecule is 433 kJ.

Orbital Overlap Let us now see how to express the idea of electron sharing in terms of orbitals. When the two atoms are far apart as in Fig. 6.2b the two 1s orbitals— and hence the two electrons—occupy different regions of space. Sharing of two electrons under these conditions is obviously impossible. In Fig. 6.2d, the atoms are near enough for the orbitals to overlap partly. The two electrons can therefore be shared under these conditions. We conclude that orbital overlap is necessary for the electrons to be shared (i.e., for a chemical bond to be formed). We have earlier seen that if two electrons occupy the same region of space then their spin quantum number must be different according to the Pauli principle. We can, therefore, also conclude that the two electrons forming the bond must have opposite spins.

Why only H_2 molecule? It is most interesting that the few simple principles discussed above in the case of the H_2 molecule are sufficient to explain and predict a whole range of chemical facts. Let us consider the question:"Why are there no molecules like H_3, H_4, etc.?" The answer is obvious. The orbital overlap which led to the formation of the H_2 molecule has used up both the available electrons to form the

covalent bond. No additional electrons being left over, the H_2 molecule has no capacity for bonding with more hydrogen atoms. Therefore, only H_2 exists but not H_3, H_4, etc. Indeed, the presence of only a single electron in the hydrogen atom implies the formation of a single bond. We thus have a straightforward explanation of the well known fact that hydrogen atoms are always univalent.

Why not He_2 molecule?: An interesting fact is that whereas hydrogen gas consists of diatomic hydrogen molecules, helium gas (helium is the element after hydrogen in the periodic table) consists only of helium atoms. What prevents helium atoms from forming molecules? The orbital overlap criterion and the Pauli principle immediately provide the answer. The $1s$ orbital in a hydrogen atom is only half-filled. Overlap with another half-filled orbital is therefore possible as sharing of the two electrons with opposite spins does not violate the Pauli principle. In a helium atom the $1s$ orbital is already full. The exclusion principle therefore forbids overlap with the $1s$ orbital of another helium atom. Helium is, therefore, a monatomic gas

6.3.2 Some Simple Molecules

We shall now take up a systematic discussion of molecules formed by atoms of the second row elements of the periodic table. Our objectives are to illustrate further applications of the principles developed so far.

It is useful at this stage to introduce a pictorial notation which simplifies the discussion of chemical bonding. We shall indicate orbitals by square boxes of the type, ☐ Orbitals will be arranged in the order of increasing energy as follows:

The cluster of three $2p$ boxes represent the three $2p$ orbitals of equal energy. An empty box ☐ means a vacant orbital, a box with a single arrow (⬆) means a singly occupied orbital, while a box with two arrows (⬆⬇) means a doubly occupied orbital.* In this notation, a single hydrogen atom can be shown as·

---
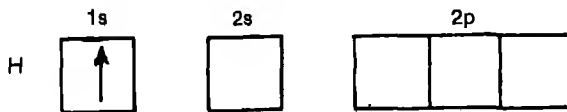
* A single electron in one orbital can have either up-spin or down-spin, the direction of a single arrow in a box is therefore immaterial Two electrons in one orbital must, however, be paired in accordance with the Pauli principle. The two arrows in a box are, therefore, shown to be anti-parallel.

While a helium atom is:

1s   2s   2p

He
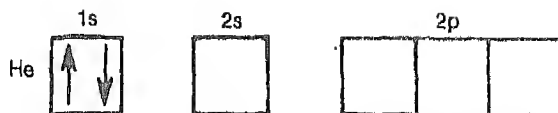
Overlap between orbitals, and hence bond formation, will be shown by enclosing the appropriate orbitals within a rectangle. The picture for a hydrogen molecule is now given as:

1s   2s   2p

H

1s   2s   2p

H
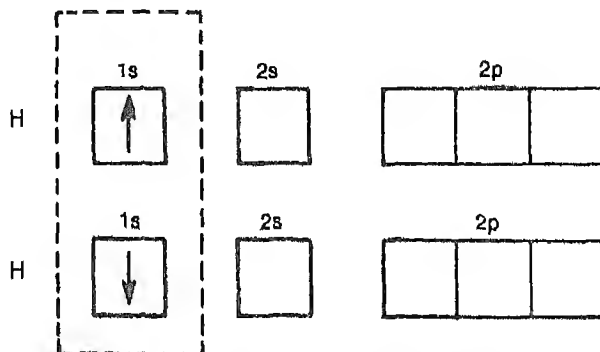
Fluorine Molecule: Let us consider a fluorine molecule. A fluorine atom has the configuration $1s^2 2s^2 2p^5$, which in the pictorial notation becomes:

1s   2s   2p

F
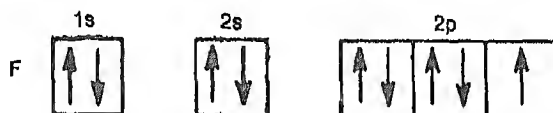
One of the 2p orbitals is only half-filled. A fluorine atom can join with another fluorine atom through the overlap of the two half-filled 2p orbitals resulting in sharing of an electron pair.

1s   2s   2p

F

1s   2s   2p

F
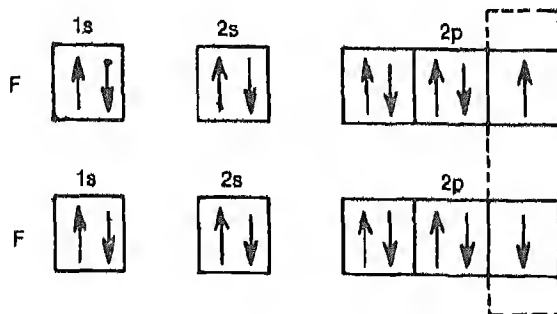
The formation of a fluorine molecule is quite similar to the formation of a hydrogen molecule. In both the cases, a single bond exists due to sharing of a pair of electrons. The difference is that in F_2, the sharing results from the overlap of $2p$ orbitals while in H_2 the overlap is of two $1s$ orbital. There is another similarity in the two cases. As in the case of hydrogen, by sharing another election, each hydrogen atom acquires two electrons, which is the maximum capacity of the $1s$ orbital. By sharing another electron, each fluorine atom similarly acquires eight electrons which is the maximum capacity of the four orbitals with $n = 2$ quantum number.

HF Molecule: A fluorine atom can also share its unpaired electron with that of a hydrogen atom. The overlap in this case is between the $2p$ orbital of fluorine and the $1s$ orbital of hydrogen

$$H\cdot + \cdot\ddot{F}\colon \rightarrow H\colon\ddot{F}\colon$$
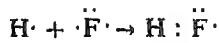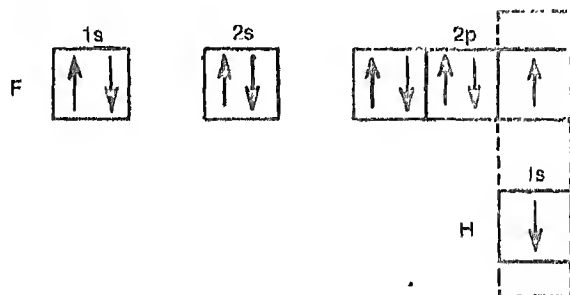
Electronegativity: The electron pair in HF is not equally shared because the two atoms are different. The sharing in H_2 and also in F_2, is equal because both the atoms are the same. A chemical bond in which the electron pair is not equally shared is sometimes termed as polar covalent bond. It is possible to find out which atom will have a greater share of the electron pair by comparing the electronegativities of the two atoms. Electronegativity, a concept first introduced by Linus Pauling, is a measure of the attraction that an atom has for a shared pair of electrons in a molecule. The larger the value, the greater the attraction. Electronegativity values have only relative significance. We shall study in later courses how these values are constructed from experimental data. Table 6.1 gives the electronegativity values of some typical elements.

Fluorine being the most electronegative element, takes a greater share of the electron pair in an HF molecule. Thus the fluorine atom in an HF molecule acquires a fractional negative charge while the hydrogen atom acquires an equal but opposite positive charge. If we wish to stress this point we can write the hydrogen flouride

LINUS PAULING (1901-)

Linus Pauling was born in portland, Oregon, U.S.A, in 1901 He graduated from Oregon State College in 1922 and he received his doctor's degree in chemistry from the California Institute of Technology in 1925. He was offered a professorship at this institution and remained there for the rest of his academic career. Pauling did much to develop our knowledge of chemical bond. He introduced many important concepts like electronegativity and resonance. He was one of the few chemists who considered the possibility of noble gases to form compounds. He published his ideas on chemical bonding in a book entitled *The Nature of the Chemical Bond*. He was awarded the Nobel Prize in 1954 for his work on molecular structure. From 1950 onwards, Pauling devoted most of his researches to biochemical problems, including the structure of proteins, the physiological functions of antibodies, the effect of the certain blood cell anomalies, and on anaesthetics. He was one of the first to suggest that protein molecules have a helical shape. He has claimed that large doses of Vitamin C are effective in preventing common cold. After World War II, Linus Pauling became a passionate supporter of nuclear disarmament and was awarded the Nobel Peace Prize in 1962, thus becoming the fourth person in history to win two Nobel Prizes.

molecule as $H^{\delta+}-F^{\delta-}$, where '$\delta-$' means a small amount of negative charge and '$\delta+$' means a small amount of positive charge.

H_2O Molecule: Let us now consider some molecules containing an oxygen atom. This atom has the configuration $1s^2\ 2s^2\ 2p^4$. The four electrons in the $2p$ orbitals can be distributed in two ways. Which distribution has lower energy?

2p

  or
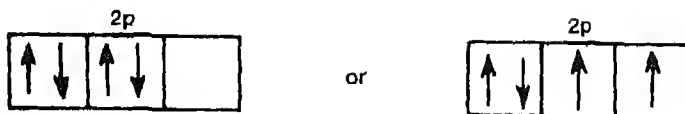
Obviously the second one. In the first, two orbitals contain two electrons each whereas in the second, one orbital contains two electrons and the other two orbitals are singly occupied. When two electrons are in the same orbital, there is naturally

TABLE 6.1

Electronegativity of Some Elements

H						
2 1						
Li	Be	B	C	N	O	F
1 0	1.5	2 0	2 5	3 0	3 5	4 0
Na	Mg		Si			Cl
0.9	1 2		1.8			3.0
K						Br
0.8						2.8
Rb						I
0 8						2.4
Cs						
0.7						

more replusion. The second possibility is therefore preferred in an oxygen atom* There are six electrons in the valence orbitals of oxygen (besides the two electrons in the inner $1s$ orbital):

1s   2s   2p

O
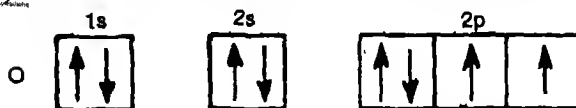
An oxygen atom can complete its octet by sharing two electron pairs. An example of this is H_2O.

What is the angle subtended by the three atoms in H_2O? The question can be answered by taking into account the directional character of p orbitals. We know that the three $2p$ orbitals are concentrated along three different directions perpendicular to each other. Thus, if one of the $2p$ orbitals is pointing along the X-axis,

---

* In the filling up of a sub-shell, an electron prefers to go to an unoccupied orbital as long as one is available rather than pairing up This rule is called Hund's rule
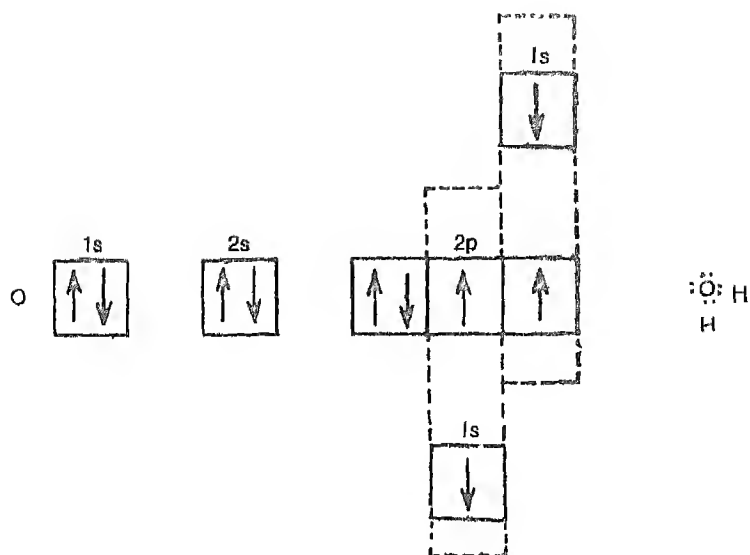
the other two must point along the Y-axis and the Z-axis respectively. In the oxygen atom we need to consider the directions of the only two of the $2p$ orbitals which are involved in bonding. These may be thought of as lying along the X and the Y axes (Fig. 6.4). Since overlap is responsible for bonding, we expect that the strongest
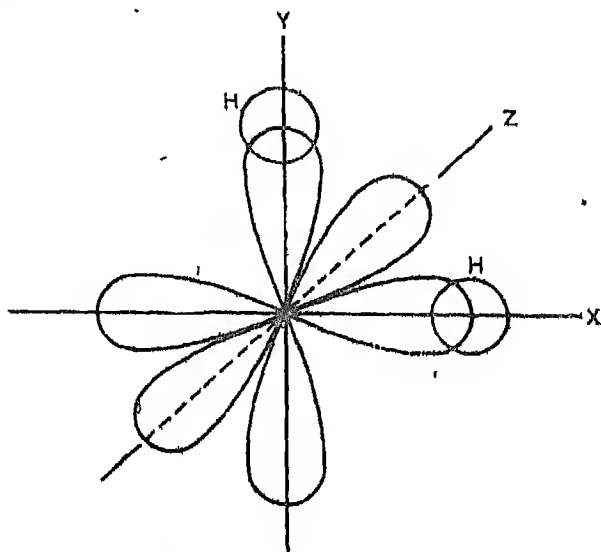
Fig. 6.4   *Orbital model of H_2O*

bond would result if the overlap is maximum The most favourable situation therefore demands that the two hydrogen atoms be placed on the X-and the Y-axes the so that each of their 1s orbitals can overlap maximally. We would therefore expect H_2O to be a bent molecule with the HOH angle of 90° Experiments confirm that the H_2O molecule is angular but the measured angle is about 104.5° It is easy to understand the reason for this discrepancy. Oxygen being more electronegative than hydrogen, charge separation occurs in each of the OH bonds The oxygen atom attains fractional negative charge and the two hydrogen atoms become positively charged e.g.,

$$(\delta+) \diagup \overset{\overset{\displaystyle(\delta-)}{O}}{\underset{H \quad H}{}} \diagdown (\delta+)$$

. Repulsion between the positive charges causes expansion of the HOH angle thus accounting for the deviation from the predicted value.

We have earlier explained the shape of the H_2O molecule on the basis of the VSEPR theory. The orbital·picture described here provides an alternate explanation of the same fact.

Our explanation of the HOH geometry applies equally well to H_2S and H_2Te because oxygen, sulphur and tellurium atoms have the same valence orbital configuration of $ns^2 np^4$. However, sulphur and tellurium atoms are larger than the oxygen atom. This means that the hydrogen atoms in H_2S and H_2Te are more separated Repulsion is therefore less. The HSH and HTeH angles are indeed experimentally found to be quite close to 90^0.

Oxygen Molecule: An oxygen atom can complete its octet by joining with another oxygen atom to form an oxygen molecule.
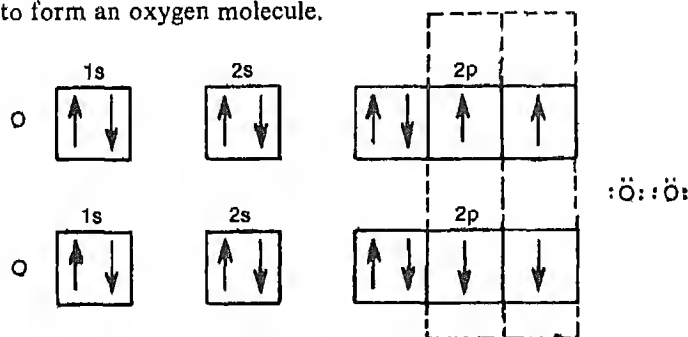
In this case, one set of $2p$ orbitals overlap as in the earlier examples but another set of $2p$ orbitals—which are perpendicular to the first set—overlap sideways. Two pairs of electrons are shared and we say that the two oxygen atoms in an O_2 molecule form a double bond. Both the electron pairs are expected to be spin paired.

Experiments show that O_2 is paramagnetic. If one pours liquid oxygen (which consists of O_2 mlecules) between the pole pieces of a magnet the liquid is attracted by the magnet showing that it is paramagnetic A similar experiment with liquid nitrogen (which consists of N_2 molecules) shows that N_2 is non-magnetic. The

paramagnetism of O_2 is due to the presence of two unpaired electrons (i.e, two electrons have the same rather than the opposite spins). Our simple picture of O_2 is thus not entirely correct. A more accurate picture will be discussed in more advanced courses.

Nitrogen Molecule: The preferred electron distribution in nitrogen atom is:
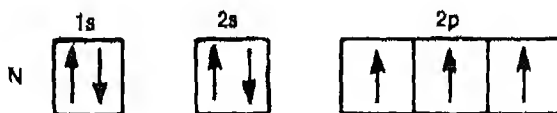
An N_2 molecule is formed by the union of two atoms such that three pairs of orbitals overlap (one pair overlaps end to end and the other two sideways).
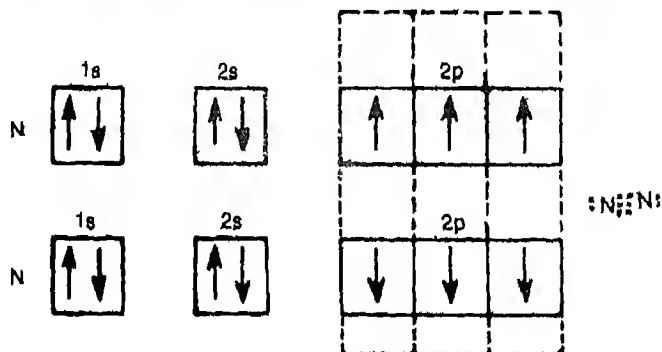
Three electron pairs are shared resulting in a triple bond in the molecule. All the electrons are spin paired. Both these features are in agreement with the observed facts

Ammonia Molecule: A nitrogen atom can also combine with three hydrogen atoms to yield ammonia, NH_3.

The directional character of the p orbitals suggests that NH_3 should be a pyramidal molecule with the three hydrogen atoms forming the base and the nitrogen atom at the apex. All the HNH angles should be $90°$. Experiments again show that though our general conclusions are correct, the angles are larger. As in an H_2O molecule, repulsion between like charges on the hydrogen atoms arising from difference in electronegativity between N and H expands the HNH angle.

6.3.3 Carbon Compounds

Carbon forms such a fascinating variety of compounds that an entire branch of chemistry, namely organic chemistry is devoted to the study of carbon compounds.

N   1s $\boxed{\uparrow\downarrow}$ 2s $\boxed{\uparrow\downarrow}$ 2p $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$

H   1s $\boxed{\downarrow}$

H   1s $\boxed{\downarrow}$

H   1s $\boxed{\downarrow}$

$$\begin{array}{c} H \\ :N: H \\ H \end{array}$$
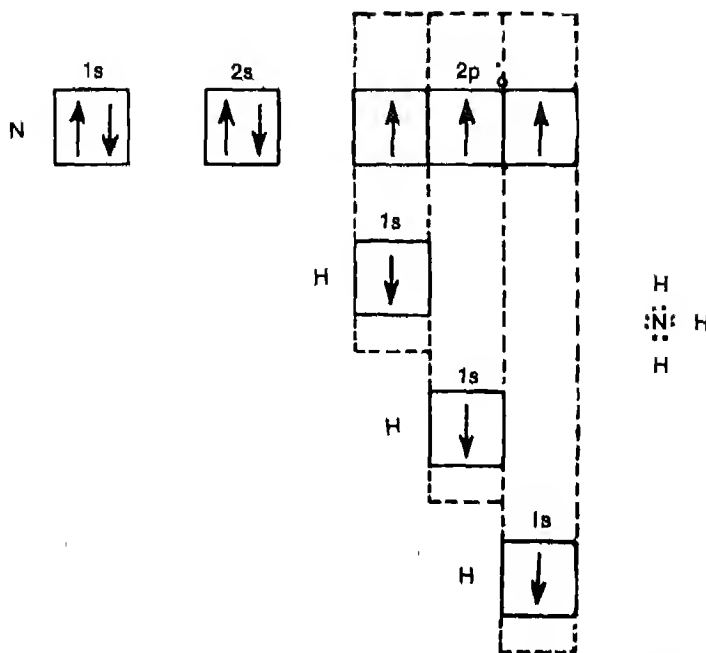
electronic configuration of a carbon atom is $1s^2\, 2s^2\, 2p^2$. This can be written as:

C   1s $\boxed{\uparrow\downarrow}$ 2s $\boxed{\uparrow\downarrow}$ 2p $\boxed{\uparrow\,|\,\uparrow\,|\,}$
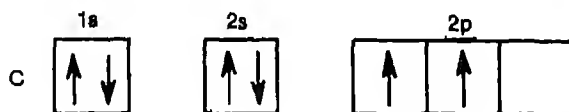
The presence of two half-filled $2p$ orbitals would lead us to expect that carbon would form divalent compounds. With hydrogen, carbon would be expected to form CH_2 as illustrated on page 178..

In fact CH_2 is very unstable and reactive. This is because the carbon atom has only a sextet (i.e., six) of electrons rather than the stable octet. In the orbital language, vacant valence orbitals, like the vacant $2p$ orbital are responsible for chemical reactivity. The overwhelming majority of carbon compounds, however, do not exhibit such instability and the carbon atoms in these compounds are always tetravalent. How can we understand the tetravalency of carbon from the electronic point of view?

We see that in the $2s$ valence orbital of carbon, there is a pair of electrons. If one of these electrons could be transferred to the $2p$ orbital (this process would require energy), there would result four partially occupied orbitals all of which can parti-

cipate in bond formation This would then yield tetravalent carbon compounds Since the formation of a bond lowers energy, the formation of four bonds would lower the energy more than that of two bonds (by a divalent carbon). This additional lowering of energy more than compensates for the energy required to transfer the $2s$ electron to the higher energy $2p$ orbital. Thus, although the transfer of an electron—usually called promotion of the electron—is by itself an energetically unfavourable process, it leads to an overall lowering because it increases the bonding capacity of the carbon atom from two to four.
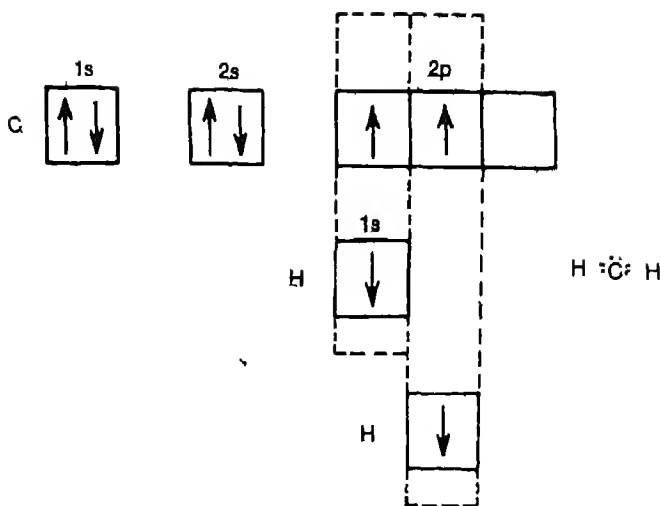
Promotion of a $2s$ electron in carbon gives the distribution, $1s^2 \, 2s^1 \, 2p^3$.
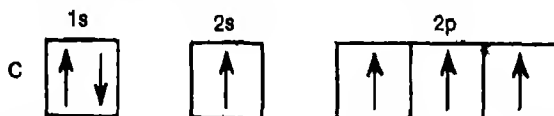
It may appear that such a distribution nicely explains the existence of a molecule like methane, CH_4, because each of the four half-filled orbitals can overlap with the four $1s$ orbitals of the four hydrogen atoms. However, there are two difficulties The above distribution predicts that in the CH_4 molecule one of the C—H bonds involving the $2s$ orbital should be different from the other three C—H bonds involving the $2p$ orbital. It also predicts that while the first C—H bond should have no preferred direction, the other three C—H bonds should be along the X-, Y-and Z-axes (i.e., perpendicular to one another). Experiments do not support either of these predictions. All the four C—H bonds in CH_4 are equivalent and are directed towards the vertices of a regular tetrahedron.

Hybridisation. We shall now introduce the concept of hybridisation which removes the two difficulties mentioned above. Hybridisation means mixing of orbitals. The idea can be clarified by an analogy. Suppose we want to paint a wall which requires four buckets of paint and we have one bucket of yellow paint and three buckets of blue paint. If we first use yellow and then the blue colour (or vice versa), the painting of the wall will be non-uniform, i.e. one fourth of it will be yellow and the rest blue In order to get paint uniformly we will first have to mix the yellow and the blue paints thoroughly. The total amount will still be four buckets which can cover the wall uniformly with the same colour (of course, the colour will now be neither yellow nor blue—it will be greenish) Whatever be the colour, the wall will have the same colour everywhere Hybridisation of orbitals is a similar concept.

sp^3 hybridisation. If one $2s$ and three $2p$ orbitals of carbon atom are mixed (hybridised), four equivalent orbitals (Fig 6.5a) will be created, which will form four equivalent bonds. These equivalent orbitals are commonly called sp^3 (pronounced es pee three) hybrid orbitals because they are formed by mixing one s and three p orbitals (Fig 6.5b). One may ask the question, "We understand how to mix paints, but how do we mix orbitals?" This is a very natural question, but unfortunately no

(a)   (b)

Fig. 6.5 (a) A single sp^3 hybrid orbital
(b) Four tetrahedrally dispersed sp^3 hybrid orbitals (formed from one s-and three p-orbitals) The smaller lobes are not shown.

satisfactory answer can be given at this stage. The 'mixing' is done in a mathematical sense, details of which can be understood in more advanced courses All that needs to be known now is that to explain the structure of a saturated hydrocarbon like CH_4 (where carbon is tetravalent), it is necessary to use four sp^3 orbitals which are pointed towards the corners of tetrahedron. These sp^3 orbitals have some features of s and some features of p orbitals. Each one of these four sp^3 orbitals forms a bond by overlapping with the $1s$ orbital of the hydrogen atom.

Consider now two carbon atoms, each with four half-filled sp^3 hybrid orbitals (Fig.6.6). One hybrid orbital of one of the carbon atoms can overlap with the hybrid orbital of the other carbon atom to form a C—C bond. The other three orbitals on each atom can be utilised to form six C—H bonds. One thus arrives at the structure of C_2H_6 (ethane). By an extension of the argument, the structure of any saturated hydrocarbon can be deduced. The structures of derivatives of saturated hydro-carbons, e.g. CH_3F, CH_2Cl_2, C_2H_5Cl can also be easily derived in a similar fashion.

Fig. 6.6 *Orbital diagram of ethane*

sp^2 *hybridisation·* The formation of sp^3 orbitals is one type of hybridisation involving one s and three p obritals Another type involves mixing of one s and only two p orbitals. This yields three hybrid orbitals called sp^2 (pronounced *es pee two*) orbitals (Fig. 6.7). The third p orbital, not used in hybridisation, is used in bond formation as a pure p orbital concentrated along one of the axes. The three sp^2 orbitals can be shown to be directed towards the corners of an equilateral triangle. This type of hybridisation can be used to explain the structure of an unsaturated hydrocarbon like, ethylene, C_2H_4.
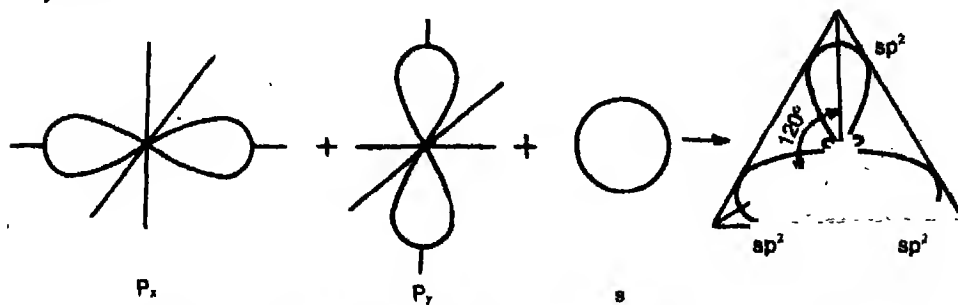
Fig. 6.7 *Formation of three sp^2 hybrid orbitals from one s-and two p-orhitals (sp² hybridisation)*

Imagine two carbon atoms, each having its half-filled sp^2 orbitals lying in a plane, and let the pure half-filled p orbital on each atom be perpendicular to this plane. An sp^2 orbital of one carbon atom can overlap with an sp^2 orbital of the other to give a C—C bond (Fig.6.8). The other two hybrid orbitals one on each atom, at an angle of 120° with the C—C axis, overlap with the four 1s orbitals of four hydrogen atoms to form four C—H bonds. The two pure p orbitals at right
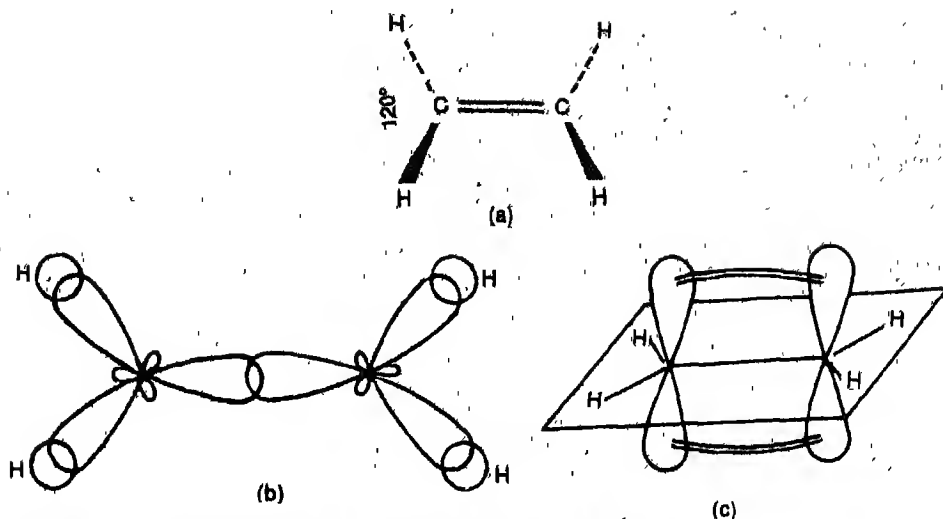
Fig. 6.8 *Bonding in ethylene:* (a) *Conventional way of showing single bonds and double bonds in ethylene* (b) *Orbital diagram for sigma bond framework* (c) *Orbital diagram for pi-bond*

angles to the sp^2 orbitals, which are parallel, overlap sideways to form a second C—C bond. We thus get a C_2H_4 molecule in which there are two bonds between the carbon atoms (i.e. a double bond C = C) and having the geometrical structure shown in the figure.

In this molecule there are two bonds between the two carbon atoms; the one formed by the overlap of sp^2 orbitals is a σ (sigma) bond while the other one formed by the overlap of the p orbitals is a π (pi) bond. In a σ bond, the orbitals overlap along the internuclear axis. The probability for finding electrons is maximum in between the two nuclei. All the C—H bonds in this molecule (and also in a molecule like methane) are σ bonds. In a π bond the orbitals overlap sideways and the probability for finding the electrons is maximum above and below the internuclear axis.

Features of π bonds: There are several features of a π bond which are easy to understand. For example, since parallel orientation of the two p orbitals is necessary
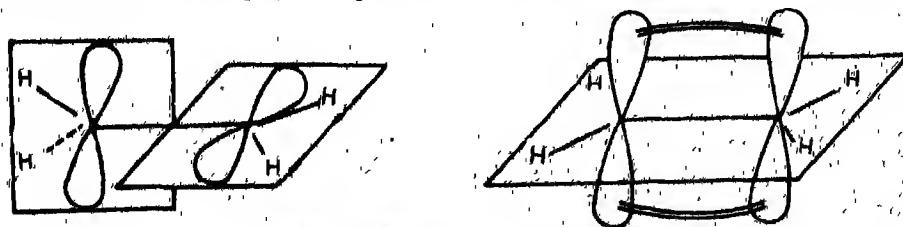
Fig. 6.9 *Lack of rotation around a π-bond*

for a proper sideways overlap (Fig.6.9), all the atoms in the C_2H_4 molecule must be in the same plane as this alone ensures that the p orbitals will be parallel. Rotation of one CH_2 fragment with respect to the other will interfere with maximum overlap of the p orbitals and therefore such rotation is prohibited.

A disubstituted ethylene like $C_2H_2Cl_2$ can exist in two forms because of the absence of rotation around the C=C bond.

In the first one, called the cis form, the chlorine atoms are on the same side while in the other—the trans form—the chlorine atoms are on opposite sides. Such cis-trans isomerism was known before the electronic theory of bonding was developed. The electronic theory however makes it clear why this type of isomerism exists.

Rotation of one CH_3 fragment against another in a C_2H_6 (ethane) molecule does not affect the overlap in a σ bond. Consequently, free rotation around a bond is always permissible. Cis-trans isomerism is, therefore, not possible in saturated organic molecules.

Another important feature of the π bond arises from the fact that the electrons in this bond are placed above and below the plane of the bonding atoms. The electrons are more exposed and are therefore susceptible to attack, especially by electron seeking (i.e. oxidising reagents). It is hardly surprising, as such, that ethylene readily reacts with oxidising agents like potassium permanganate or potassium dichromate at ordinary temperatures whereas ethane (which has only σ electrons) is totally unaffected by these reagents at normal temperatures. In general, π bonds provide the most reactive centres in unsaturated molecules. Many more chemical, biological and other characteristics of π electrons will be discussed in later courses.
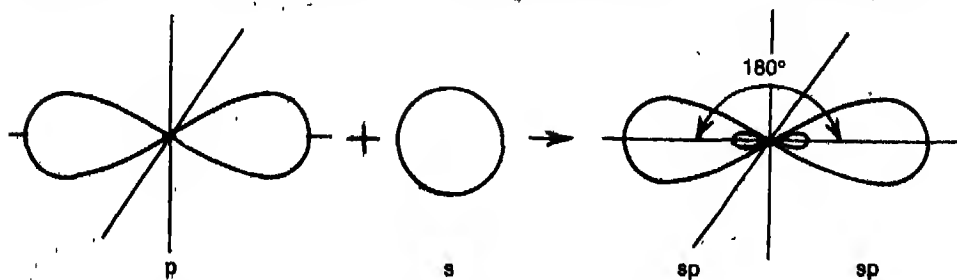
Fig. 6.10 *Formation of the two sp hybrid orbitals from one s-and one p-orbital*

sp Hybridisation: There exists one more type of hybridisation involving the *s* and *p* orbitals called the *sp* hybridisation. Here, one *s* orbital and one *p* orbital are mixed together to give two *sp* (pronounced *es pee*) hybrids leaving two *p* orbitals as such (Fig 6.10) The two *sp* hybrid orbitals are directed opposite to each other, i.e they make an angle of 180° with respect to each other. The linear structure of a molecule like C_2H_2 (acetylene) is easily explained on the basis of *sp* orbitals, the overlap between one *sp* orbital from each atom will give one C—C bond of the σ type (Fig. 6.11) The other *sp* orbital on each atom pointing in the opposite direction is utilised
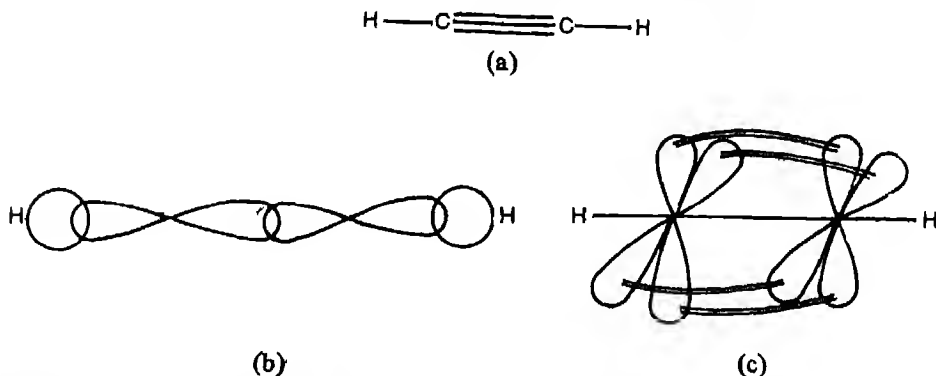
Fig. 6.11 *Bonding in acetylene (a) Conventional way of showing single bonds and triple bonds in acetylene (b) Orbital diagram for sigma bond framework (c) Orbital diagram for triple bond*

in the formation of a C—H bond. We are now left with four pure *p* orbitals, two on each atom They form two sets of parallel *p* orbitals at right angles to each other and also to the σ bonds. Within each set, sideways overlap can take place giving two π bonds. Thus, acetylene should have a triple bond (one σ and two π). Whenever there are multiple bonds between any two atoms, one of them would be a σ bond the others would be π bonds. For example, in the O_2 molecule, discussed earlier, there is one σ and one π bond, and in the N_2 molecule there is one σ and two π bonds.

In the third row elements, valence orbitals include the *s* and *p* as well as the *d* orbitals. Many hybridisation schemes are possible with the help of these orbitals which explain octahedral, square planar and other molecular shapes observed in nature. The chemistry of transition elements is particularly dominated by the hybrid orbitals formed from the *s, p* and *d* orbitals.

6.3 4   Boron and Beryllium Compounds

Having considered the carbon atom in some detail, let us now turn our attention to the boron atom. This atom has the configuration $1s^2 \, 2s^2 \, 2p^1$ Promotion of a $2s$ electron should be favoured as it would make available three electrons for bonding.

The inequivalence of the $2s$ and the $2p$ orbitals can be removed by forming sp^2 hybrid orbitals. It follows that in a molecule like BF_3 formed by the overlap of sp^2 hybrid orbitals of boron and the p orbitals of fluorine atoms the three B-F bonds should make an angle of 120° with each other—a prediction fully verified by experiments.

In beryllium atom $(1s^2 2s^2)$,, promotion of one $2s$ electron to the $2p$ orbital permits the possibility of sp hybridisation. The two sp orbitals being oriented in opposite directions, a molecule like BeF_2 should be linear as observed.

6.4   THE COORDINATE COVALENT BOND

In all the examples considered so far, the two atoms involved in covalent bonding contribute one electron each to form the shared electron pair. A covalent bond, however, can also result if only one of the atoms contributes both the electrons. Such a covalent bond is referred to as a coordinate covalent bond or simply as a coordinate bond.

Sulphuric acid (H_2SO_4) provides a simple example of the coordinate bond. The Lewis structure of this molecule is shown below:

$$
\begin{array}{c}
\ddot{\text{O}}\!:\\[-2pt]
{}^{\times\times}\\[-4pt]
\text{H}\!:\!\overset{\times}{\underset{\times}{\text{O}}}\text{ S }\overset{..}{\underset{\times\;\times}{\text{O}}}\!:\!\text{H}\\[-2pt]
:\ddot{\text{O}}\!:
\end{array}
$$
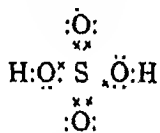
For clarity, we have indicated the valence electrons of the sulphur atom by crosses (×) while those of the oxygen and the hydrogen atoms are shown as usual by dots. It can be seen that the bonds between the sulphur atom and the oxygen atoms of the OH group are of the normal covalent type, each atom contributing one electron to the shared pair. (The pair consists of a cross and a dot, the cross coming from the sulphur atom and the dot from the oxygen atoms. The bonds between the sulphur atom and the other two oxygen atoms also involve electron pairs but in this case, the shared pair consists of two crosses, i.e. both the electrons come from the sulphur atoms. These two bonds are of the coordinate covalent type. To distinguish between the two types of covalent bonds H_2SO_4 is often written as

$$
\begin{array}{c}
\text{O}\\[-2pt]
\uparrow\\[-4pt]
\text{H}\!-\!\text{O}\!-\!\text{S}\!-\!\text{O}\!-\!\text{H}\\[-4pt]
\downarrow\\[-2pt]
\text{O}
\end{array}
$$
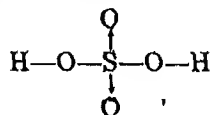
where the lines represent covalent bonds and the arrows represent coordinate bonds. The arrow indicates that the sulphur atom has donated an electron pair to the acceptor oxygen atom. (The coordinate bond, for this reason, is also called a dative bond or a donor—acceptor bond.)

There are many examples where two (or more) stable molecules combine to yield a molecular complex. A coordinate bond is usually responsible for holding the two molecules together in such complexes. Let us reconsider the molecules NH_3 and BF_3 The electron dot structures of these molecules are.

$$
\begin{array}{cc}
\text{H} & \text{.F.} \\
\text{H·N.} & \text{B.F:} \\
\text{H} & \text{:F.}
\end{array}
$$

The nitrogen atom has a full octet around it but the boron atom has only a sextet. A coordinate covalent bond in which the unshared electron pair is donated by the nitrogen atom permits the boron atom to acquire the octet. The ammonia-boron trifluoride molecular complex can be shown as

$$
\begin{array}{ccc}
& \text{H} & \text{F} \\
& | & | \\
\text{H—N} & \longrightarrow & \text{B—F} \\
& | & | \\
& \text{H} & \text{F}
\end{array}
$$
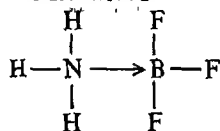
Coordinate bonds are involved in the formation of transition metal complexes also known as coordination compounds. Examples of such molecules will be dealt with in later courses.

6.4.1 Ionic Bond as an Extreme Case of Polar Covalent Bond

We have earlier mentioned the fact that if two atoms with different electronegativities are bonded, the atom with greater electronegativity has the greater share of the electron pair. In LiF, the difference in electronegativity is so large that the fluorine atom is almost in complete possession of the electron pair. It is more appropriate in such circumstances to say, that an electron has been transferred from the lithium atom to the fluorine atom. We know that loss of an electron by a lithium atom means formation of the Li^+ ion, while gain of an electron by a fluorine gives a F^- ion Thus, transfer of an electron from lithium to fluorine amounts to the formation of the Li^+F^- ion pair. In such an ion pair, we have ions (positive and negative), and not atoms, held together by mutual attraction or what is known as an ionic bond An ionic bond is an extreme case of a polar covalent bond. It results when the sharing is so unequal that it is more convenient to regard one of the electrons as transferred from one atom to the other.

Energy considerations involved in an ionic bond are worth examining from another angle. To remove an electron from an atom, the energy needed is the ionisation energy of the atom. The ionisation energy of alkali metal atoms is low, meaning that comparatively less energy is needed for removing the valence electron Atoms like the halogens have an attraction for electrons. Such atoms release energy

(the energy released is called electron affinity) on acquiring an electron. It turns out that the electron affinity of a fluorine atom is lower than the ionisation energy of a lithium atom. The electron transfer from the lithium to the fluorine atom is not favoured energetically. However, the Li^+F^- ion pairs are indeed formed. This is due to the fact that the electrostatic attraction between the two opposite charged ions (Li^+F^-) more than compensates the energy difference between the ionisation energy of Li and the electron affinity of F.

In case one wonders why attraction does not lead to a merger of the two ions, one should recollect that there are repulsive forces between the nuclei of the two ions and between the electrons of the two ions. If the ions come very close, repulsion outweighs attraction and pushes the ions out. If the ions are far apart, attraction outweighs repulsion and pulls the ions in. Equilibrium is achieved at such separations where the attractive and repulsive forces balance each other. Other examples of ionic bonds are Na^+Cl^-, K^+F^- and K^+Cl^-.

It was stated earlier that a molecule is formed when a group of atoms acquire stability through lowering of energy. We have now seen two mechanisms by which lowering of energy is achieved In one case, an electron pair is shared (covalent bond); in the other case an electron is transferred, the resulting ions being held together by mutual attraction (ionic bond). In between the two extremes lies the polar covalent bond which is partly covalent and partly ionic. It is possible to estimate the percentage of ionicity—also called the ionic character—of a polar covalent bond from experimental data. It may be noted that bonds in molecules are always of the polar covalent type since hundred per cent covalent or hundred per cent ionic bonds are not known However, a polar covalent bond which is predominantly ionic (i.e., having 50 per cent ionic character or more) is normally called ionic Similarly, the one with a predominantly covalent nature (i.e., less than 50 per cent ionic in character) is commonly known as covalent.

6 4.2 Ionic Character of Bonds and Polar Molecules

A simple method for calculating the percentage ionic character of bonds is based on the measurement of the dipole moment. When a positive charge is separated from a negative charge, the pair of opposite charges is called dipole For example, a molecule like HF behaves like a dipole. It is useful to introduce a quantity called the dipole moment which is equal to the charge on either of the atoms (both charges are equal) multiplied by the distance between them. The dipole moment has a direction which is conventionally indicated by drawing an arrow—the tail of the arrow is placed on the positive end and the head on the negative end. Thus, the dipole in HF is represented as,

The dipole moment of a molecule can be experimentally measured. Let us suppose that we are able to determine the dipole moment of HF and let us also suppose that we know the distance between the two ions. From the definition of the dipole moment (charge $\times$ distance) it follows that we can calculate the exact charge on either atom. If an electron is fully transferred from one atom to another, this charge will be equal to the electron charge However, if the transfer is partial, then the charge calculated from the dipole moment must be less than the electron charge. The ratio ' of the actual charge to the electron charge immediately provides an estimate of the ionic character

In molecules containing more than one bond, the dipole idea can be applied to individual bonds within a molecule It is then known as bond dipole. A bond between atoms with different electronegativities must obviously have a dipole associated with it. However, whether a molecule as a whole possesses a dipole moment or not depends upon the relative orientation of the bond dipoles. Thus the dipole moment provides useful information about molecular shapes as the following examples show.

The dipole moment of the BeF_2 molecule is found to be zero. Different electronegativities of beryllium and fluorine atoms means that the Be-F bond must have a bond dipole. How can the two bond dipoles be placed so that the net effect is zero? If equal arrows are pointing in opposite directions, their sum is zero (Fig 6.12). BeF_2 must therefore be a linear molecule as stated earlier.

bond dipoles   total dipole moment

Fig. 6.12 *Dipole moment diagram of BeF₂ (a nonpolar molecule)*

The triatomic H_2O molecule has a dipole moment. This fact immediately rules out the linear structure H-O-H and proves that H_2O is angular (Fig. 6 13). Molecules having a dipole moment are known as polar molecules.

BF_3 also has a zero dipole moment but B-F has a bond dipole. The three arrows shown in Fig. 6.14 give a net sum of zero because the resultant of any two (by the law of parallelogram of forces) is equal and opposite to the third. The three fluorine atoms must therefore be at the vertices of an equilateral triangle with the boron atom at the centre.

The tetrahedral structure of CH_4 gives zero dipole moment as the internal dipoles associated with the individual bonds, $C^\delta-H^\delta$ (which have small but finite dipole moment) neutralise each other
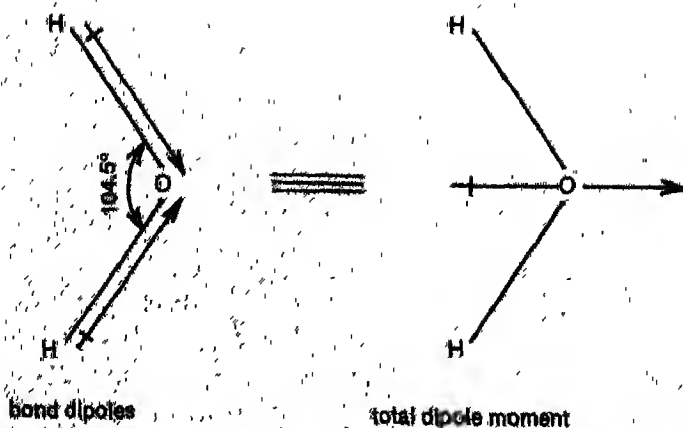
Fig. 6.13 *Dipole moment diagram of* H_2O *(a triatomic polar molecule)*
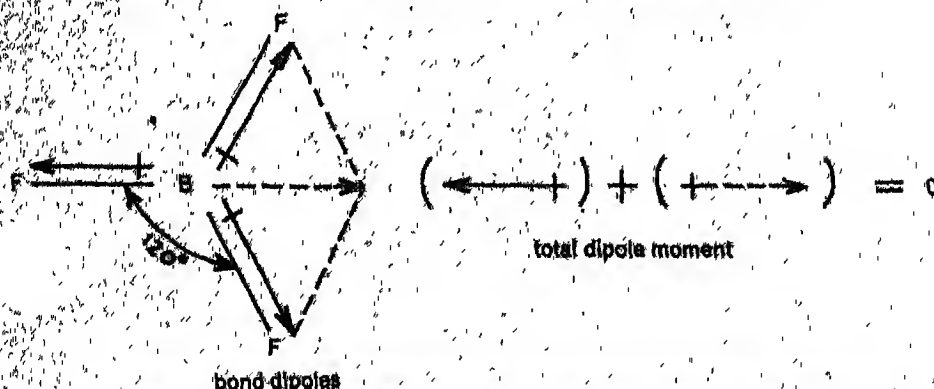
Fig. 6.14 *Dipole moment diagram of* BF_3 *(a tetra atomic non-polar molecule)*

6.5   BONDING IN SOLID STATE

Covalent and ionic bonds are the only possibilities in isolated molecules. Molecules are sufficiently isolated from one another only in the gaseous (or vapour) state. In liquids and solids—which may be collectively called as the condensed state—not only does one observe covalent and ionic substances but also substances characterised by the so-called metallic bond and van der Waals' bond. We shall briefly examine bonding in the condensed state, with special reference to the solid state.

A solid or a liquid is really a cluster of molecules. The difference in solid and liquid clusters is mainly of ordering. Solid clusters are regular (ordered) while liquid clusters are irregular (disordered) However, both types of clusters are formed

because energy is lowered by such cluster formation. We have seen how the energy of a group of atoms is lowered through covalent and ionic bonding. We will now see how the energy of clusters of molecules is lowered through various kinds of bonding.

Ionic solids: Consider a large number of Li^+F^- ion pairs in the vapour phase. As the temperature is lowered or pressure is increased, we expect lithium fluoride vapour to condense. What arrangement of Li^+F^- ion pairs would correspond to lowest energy? Naturally, an arrangement in which every F^- is surrounded by as many Li^+ as possible and every Li^+ is surrounded by as many F^- as possible. The number of oppositely charged ions that surround a particular ion depends upon the relative sizes of the positive and the negative ions. For example, in lithium fluoride (or sodium chloride), each Li^+ (or Na^+) ion has six F^- (or Cl^-) as nearest neighbours and F^- (or Cl^-) is surrounded by six Li^+ (or Na^+) ions (Fig. 6.15). Such a regularly ordered three-dimensional array is called a crystal. A crystal with ions as units is called an ionic crystal. Substances like lithium fluoride, sodium chloride and potassium chloride exist in solid state as ionic crystals. Positive and negative ions are the units out of which ionic crystals are formed. These units are held together by attractive forces between the oppositely charged ions. One can alternatively say that an ionic crystal is held together by ionic bonds.
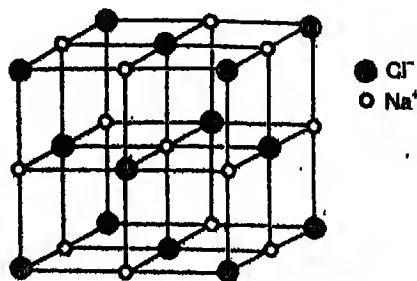
Fig. 6.15 *Structure of NaCl (ionic solid)*

Ionic solids have generally high melting points because considerable thermal energy is needed to overcome the attraction between oppositely charged ions. In the molten state, the regular arrangement of a crystal is destroyed but on an average, a positive ion is surrounded by a number of negative ions and vice versa. Ionic substances conduct electricity in the molten state because the ions are free to move. However, ionic solids do not conduct electricity since ions are not free to move in the crystals. Ionic solids dissolve easily in polar solvents like water.

Molecular Solids: We have seen earlier that a molecule like H_2 cannot form additional covalent bonds because the bonding capacity of both the atoms is saturated. However, the fact that hydrogen gas, which consists of H_2 molecules, liquifies and even solidifies at low temperatures implies that attractive forces must be present between H_2 molecules. The origin of such attractive forces can be understood in the following manner.

Let us consider a helium atom. The most favourable arrangement of the two electrons is as shown in Fig. 6 16a where the electrons are located diametrically opposite to each other and the centres of positive and negative charges coincide. The probability of such a configuration is maximum. However, because an electron in an atom or a molecule does not have a fixed position, other configurations are also possible (Fig 6 16 b,c) in which at a particular instance the electronic distribution is not symmetrical, i.e. the centres of positive and negative charges do not coincide. The instantaneous unsymmetrical distribution of electrons in the atom will set up a dipole. This dipole induces a dipole in neighbouring atoms and a force of attraction results. This force is usually called van der Waals' force (in honour of the Dutch chemist J.H. van der Waals who first studied their nature). Van der Waals' forces are responsible for the condensation of inert elements, and gases like hydrogen, nitrogen, oxygen, methane, etc , which also have no residual bonding capacity. In all such cases, liquid and solid clusters form only through the van der Waals' type of interaction This interaction is very much weaker than the covalent interaction responsible for molecule formation. Van der Waals' solids have molecules as individual units. Such solids are, therefore, generally known as molecular solids.
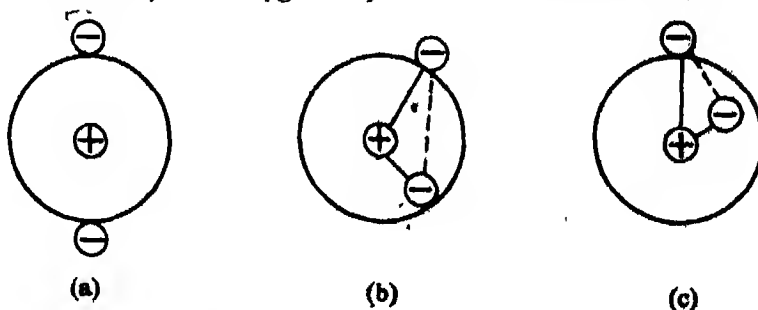
Fig. 6.16 *van der Waals forces between helium atoms:* **(a)** *shows symmetrical distribution of the two electrons;* **(b)** *and* **(c)** *show two unsymmetrical distribution of the two electrons (in both these configurations, helium atom has a transient dipole moment responsible for van der Waals forces)*

Molecular solids are soft, have low melting and boiling points, and high vapour pressure These features are due to the weakness of the van der Waals' forces. Molecular solids have very low solubility in solvents like water containing polar molecules.

Covalent Solids: In a covalent solid, atoms are connected to one another by covalent linkages forming a giant network. The units in these networks can either be atoms of the same element or atoms of different elements with similar electronegativities. Diamond and silicon carbide (SiC) are two examples of covalent solids. In diamond (Fig. 6.17) each carbon atom is linked to four other carbon atoms through the four tetrahedrally oriented covalent bonds thus forming a three dimen-

sional network of carbon atoms. Each bond is formed by the overlap of two sp^3 hybrid orbitals located on neighbouring atoms SiC has the same three dimensional arrangement as diamond with each silicon atom surrounded by four carbon atoms and each carbon atom surrounded by four silicon atoms. Since covalent bonds are strong and directional, solids of this type are very hard (diamond is the hardest substance known), have high melting and boiling points, and resist deformation
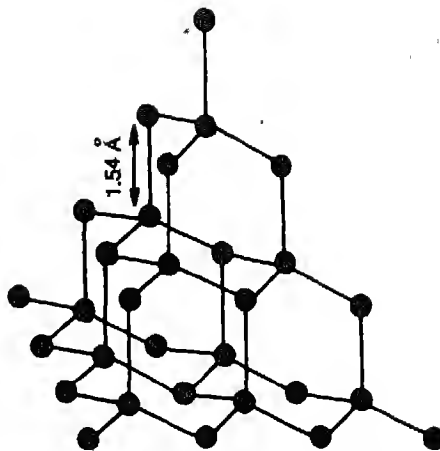
Fig. 6.17 *Structure of diamond*

In addition to diamond, the element carbon exists in another allotropic form known as graphite (Fig. 6.18) The carbon atoms in this form exhibit sp^2 hybridisation. The three sp^2 orbitals being in the same plane, the covalent bonding of each carbon atom with three other carbon atoms leads to infinite sheets. The sheets are themselves held together by the much weaker van der Waals' forces. It is quite easy for one sheet to slide over another. The layer structure of graphite thus nicely explains why it is an excellent lubricant.

Metals: Over eighty elements in the periodic table are metals. With the exception of mercury (m.p = 234 K) and gallium (m.p. = 302.8 K), metals are solids at ordinary temperatures and pressures. They are good conductors of heat and electricity and possess a lustrous appearance. Metals are ductile (i.e., can be drawn into wires) and malleable (i e , can be beaten into sheets) Their strength shows considerable variation ranging from very soft (e.g , alkali metals) to very hard (e.g., tungsten). Metals being

Fig. 6.18 *Structure of graphite*

the backbone of industry and technology, play an important role in modern civilisation. It is of great interest to examine the nature of bonding in metals and to understand how it explains the characteristic metallic properties.

It is a simple matter to see that the various bond types discussed so far are not applicable to the metallic state. For example, consider lithium. In the solid state, it is known that each lithium atom has eight nearest neighbours. The fact that a lithium atom has only one valence electron ($1s^2 2s^1$) rules out the possibility of electron pair covalent bonds with eight neighbours. The presence of only one type of atoms (and the consequent absence of electronegativity difference) rules out ionic bonding. Then, metals are obviously too strong to be held together by the weak van der Waals' forces. It is clear that we must look for a different model to explain the stability of metals.

The most elementary model of a metal visualises it to be a three dimensional array of positive ions held together by a pool of electrons, commonly known as electron sea or electron gas. The electron sea is formed from the contribution of valence electrons by each neutral atom. For example, in lithium metal, each atom contributes one valence electron to the pool, the residual Li^+ ion forming a three dimensional array or lattice. In magnesium, two valence electrons are contributed by each atom, leaving behind a lattice of Mg^{2+} ions. The lowering of energy is due to the attractive interaction between the negatively charged electron sea and the positively charged lattice. It is important to realise that the electrons in the pool are not localised in any particular region but are spread over the entire lattice. (This is the reason why the term electron gas is used to describe the behaviour of electrons in metals.) These (delocalised) electrons are free to move in all directions. Electrons are the charge carriers in metals whereas positive and negative ions are the charge carriers in ionic liquids which also conduct electricity. Because electrons are much lighter than ions, it is understandable that they have higher mobility. Electrical conductivity of metals is therefore much higher than electrical conductivity of ionic liquids.

If one end of a metal is heated, the mobile electrons transport excess thermal energy from one end to the other. Thermal conductivity is also due to the presence of delocalised electrons. The shiny appearance of metals is due to the ability of mobile electrons to absorb and re-emit electromagnetic radiation. Unlike a covalent bond, a metallic bond has no directional character. Metals can therefore be readily twisted, drawn into wires, or beaten into sheets.

6.6   THE HYDROGEN BOND

The melting and boiling points (Table 6.2) of the hydrides of the elements of groups 14, 15, 16 and 17 of the periodic table show an interesting feature. Among the group 14 hydrides, the melting and boiling points increase as the molecular mass increases.

TABLE 6 2

Melting and Boiling Points (K) of Some Hydrides

	Group 14			Group 15	
	m p.	b.p		m.p	b.p.
CH$_4$	89.0	111 5	NH$_3$	195.5	239 6
SiH$_4$	88.0	161 2	PH$_3$	138 0	185 0
GeH$_4$	108 0	183 0	AsH$_3$	159 0	218.0
SnH$_4$	123.0	221.0	SbH$_3$	184 0	256.0
	Group 16			Group 17	
	m.p	b.p		m.p	b p
H$_2$O	273.0	373 0	HF	180 7	392.4
H$_2$S	190.3	211.2	HCl	161.0	189.4
H$_2$Se	209.0	231.0	HBr	184 5	206 0
H$_2$Te	222.0	271 0	HI	222 2	237.0

This is because a heavier molecule usually contains more electrons and van der Waals' attraction increases with the number of electrons. However, hybrides of 15, 16, and 17 group elements do not show this pattern In each of these groups, the first member of the series (NH$_3$, H$_2$O or HF) shows abnormally high melting and boiling points. This clearly indicates that in the condensed state of these hybrides, some attractive interaction over and above the van der Waals' attraction must be present. This interaction has been traced to the ability of the hydrogen atoms in such molecules to form hydrogen bonds. Let us consider the HF molecule to understand the nature of the hydrogen bond.

Fluorine being the most electronegative element, the electron pair in HF belongs largely to the fluorine atom. The fluorine atom thus acquires large partial negative charge and the hydrogen atom a corresponding positive charge. The positive hydrogen attracts the negative end of another HF unit. Such a combination is called a hydrogen bond and is shown as a dotted line (...). For example, hydrogen bonding in HF is shown as: H — F ... H — F. Hydrogen bonding at either ends permits the above pair to link with additional HF units. Liquid hydrogen fluoride consists of clusters of HF molecules held together by hydrogen bonds. The high boiling point of HF, compared to those of the other hydrogen halides, arises from the fact that energy is needed to break the hydrogen bonded clusters

The abnormal melting and boiling points of NH$_3$ and H$_2$O are also due to the formation of hydrogen bonds. Nitrogen and oxygen atoms in these molecules do not

pull electrons as strongly as a fluorine atom, but they are sufficiently electronegative to enable the formation of hydrogen bonds

Water is the most familiar substance which exhibits hydrogen bonding. The hydrogen bond here is of the O—H ...O-type. It is so extensively hydrogen bonded that in the liquid state there are hardly any free H_2O molecules. Each water molecule is generally hydrogen bonded to four other water molecules (Fig. 6 19). Ice is a hydrogen bonded crystal The three dimensional arrangements of biologically important porteins and nucleic acids are also essentially determined by the hydrogen bonds in them.
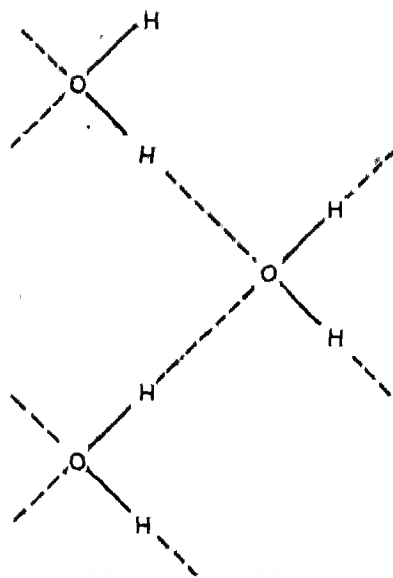
Fig. 6.19 *Hydrogen bonding between water molecules*

The strength of a hydrogen bond is typically between 3.5 kJ mol^{-1} to 8 kJ mol^{-1} It is thus considerably weaker than the average covalent bond and much stronger than the van der Waals' interaction.

6.7 RESONANCE

Consider the molecule O_3 (ozone). Its structure can be written as
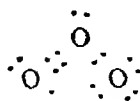
where each oxygen atom has an octet of electrons. The structure shows the presence of one double bond and one single bond, i.e., $O=O\diagdown O$. Since double bonds are shorter than single bonds. we would expect the two bond lengths in this molecule to be unequal. However experiments not only show that the bond lengths are equal but also that the bonds are intermediate between single and double bonds. It is obvious that for a molecule like O_3, a single Lewis structure is insufficient to account for the observed facts. The difficulty is solved if we realise that an alternating Lewis structure can also be written:

In this case, the double and the single bonds are interchanged Since neither of the two above Lewis structures of the ozone molecule can individually explain its properties, it is assumed that the actual structure is in between the two The individual structures are called resonance structures or canonical forms and the molecule is represented as resonance hybrid.
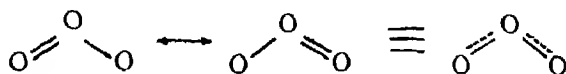
A doubly headed arrow (⟷) represents resonance between two canonical forms.

Resonance structures have no physical reality in the sense that neither of the two ozone structures can be prepared in the laboratory. Such structures exist in imagination only. The need for the resonance concept arises because there are many molecules like O_3, whose behaviour cannot be represented by a single Lewis structure. The resonance concept is particularly useful to explain features of unsaturated compounds in organic chemistry.

EXERCISES

6.1   Deduce the empirical formulas and draw the Lewis structures for the ionic compounds formed by the following pairs of elements.
Na, O; K, S; Na, P; Mg, Br; Al, F; Ca, O; Li, S

6.2   Draw the Lewis symbols for the following elements.
Na, Ca, B, Br, Xe, As, Ge

6.3   Draw Lewis structures for the following molecules and ions.
F_2, PH_3, H_2S, $SiCl_4$, C_3H_8, F_2O, Na^+, Br^-

6.4   Three elements have the following Lewis symbols

A·   ·Ḃ·   :Ç·
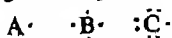
(i)   Place the elements in the appropiate group of the periodic table.
(ii) Which elements are likely to form ions? What is the expected charge on the ions?
(iii) Write the formulas and the Lewis structures of the covalent compounds formed between (a) A and B and (b) A and C.

6 5   Identify the atoms in each of the following compounds which do not obey the octet rule.

SO_2, SF_2, SF_4, SF_6, OF_2, BCl_3, PCl_3,

6.6   Predict the shapes of the following molecules using the valence shell electron pair repulsion (VSEPR) theory.
$BeCl_2$, $SiCl_4$, AsF_5, H_2S, $HgBr_2$, PH_3, GeF_2

6.7   Discuss how the valence bond theory explains the shapes of the following molecules
BeF_2, H_2O, NH_3, CH_4

6.8   (i) Draw the shapes of the following hybrid orbitals
sp, sp^2, sp^3
(ii) Explain the difference between a σ bond and a π bond.

6.9   Explain how the valence bond theroy accounts for.
(i) a carbon-carbon double bond
(ii) existence of cis-trans isomers

6.10 The molecule SO_2 has a dipole moment. Is the molecule linear or bent? Explain your reasoning.

6.11 Predict the dipole moment of
(i) a molecule of the type AX_4 having a square planar geometry.
(ii) a molecule of the type AX_5 having a trigonal bipyramidal geometry.
(iii) a molecule of the type AX_6 having an octahedral geometry.

6.12 You are given the electronic configurations of five neutral atoms—A,B,C,D and E.
$A—1s^2 2s^2 2p^6 3s^2$
$B—1s^2 2s^2 2p^6 3s^1$
$C—1s^2 2s^2 2p^1$
$D—1s^2 2s^2 2p^5$
$E—1s^2 2s^2 2p^6$
Write the empirical formula for the substances containing.
(i) A and D,   (ii) B and D,   (iii) only D,   (iv) only E.

6.13 Rhombic sulphur is a crystalline yellow solid which dissolves in CS_2 but is insoluble in water. It does not conduct electricity It melts at 386K to give a clear straw coloured liquid. The liquid also does not conduct electricity Its viscosity is comparable to that of water. Which of the following structures would be most likely to explain the properties of the solid form and of the liquid form?
(i) an ionic solid of S^+ and S^- ions
(ii) a metallic crystal of sulphur atoms
(iii) a molecular crystal of S_8 molecules
(iv) a network crystal of sulphur atoms
(v) an ionic liquid of S^+ and S^- ions
(vi) a molecular liquid of S_8 molecules
(vii) a metallic liquid like mercury

6.14   Consider each of the following in the solid state.
        (i) methane   (ii) caesium chloride   (iii) germanium   (iv) lithium   (v) argon   (vi) ice
        State which would be an example of.
        (a) a high melting, network solid;
        (b) a non-conducting solid which becomes a good conductor in the molten state;
        (c) a solid with high electrical and thermal conductivity,
        (d) a low melting solid held together by van der Waals' forces;
        (e) a solid in which hydrogen bonding exists.

UNIT 7

CARBON AND ITS COMPOUNDS

Carbon forms more compounds
than all the other elements put
together

OBJECTIVES

In this Unit we shall learn

* the basic features of the chemistry of carbon and its compounds like oxides, halides and carbides; .

* the reasons for the multiplicity of organic compounds and the need to study organic compounds separately.

* the IUPAC procedure for naming organic compounds;

* the importance of different classes of organic compounds in everyday life.

ALTHOUGH CARBON RANKS seventeenth in the order of abundance in the earth's crust, it forms the largest number of compounds, next only to hydrogen. Carbon and its compounds are widely distributed in nature. Diamond and graphite are the two different forms of pure elemental carbon present in nature. Charcoal and coke are impure forms of carbon. They are obtained by strong heating of wood and coal in the absence of air, respectively. In the combined state, carbon is present as carbonate in many minerals. In air, carbon dioxide is present in small quantities.

All living systems contain carbon compounds. Indeed, life as we know today, would be impossible without them. Fossil fuels such as lignite, coal and oil which are derived from living matter are all rich in carbon compounds

7.1 ELEMENTAL CARBON

The phenomenon of existence of different forms of an element is called ALLOTROPY Diamond and graphite, the two different forms of naturally occurring elemental carbon, are allotropes. Due to their different structures (Figs. 6.17 and 6.18), they have different properties

In diamond, each carbon atom is linked tetrahedrally to four neighbouring carbons in an sp^3 hybridised manner This network extends in three dimensions and is very rigid. Diamond is therefore a very hard substance In graphite, on the other hand, each carbon is attached to three neighbouring carbons to form a sheet of hexagons, with sp^2 hybridisation Thus, out of the four bonding electrons in carbon, only three are used and the fourth is free, enabling graphite to be a conductor. The hexagonal sheets of graphite are held together by weak van der Waals' forces, this enables one sheet to slide over another and accounts for the lubricating properties of graphite. While diamond is very hard, transparent and a non-conductor of electricity, graphite is soft, opaque and a good conductor of electricity. Another form of graphite is carbon black. This is not present in nature. It is obtained by burning compounds of carbon and hydrogen in a limited supply of air. Diamond is employed where hardness is desired, like in drilling bits and abrasives Graphite finds use as a lubricant and in dry cells. Carbon black in used to harden rubber for tyre manufacture. The less pure forms of the elemental carbon—charcoal and coke, are widely used as fuels. Coke is also used as a reducing agent in metallurgy.

7.2 CARBON COMPOUNDS

Carbon compounds can be broadly classified into two categories. (a) those containing carbon bonded to other atoms like oxygen, halogens, metals and not having carbon-carbon bonds, and (b) those compounds having carbon-carbon bonds For historical reasons, compounds of type (a) are generally known as inorganic compounds. Compounds of type (b) are called organic compounds. This classification is applicable to most carbon compounds.

7.3 INORGANIC COMPOUNDS OF CARBON

Carbon readily combines with a variety of elements to form binary compounds such as oxides, halides and carbides. Carbonates and bicarbonates are salts of the unstable carbonic acid, H_2CO_3, which decomposes to carbon dioxide and water.

7.3.1 Oxides of Carbon

Carbon when burnt in air or oxygen forms two oxides, carbon monoxide, CO and carbon dioxide CO_2 Carbon monoxide is formed, by incomplete combustion of carbon or carbon containing fuels. It is present, for example, in automobile exhausts

$$C + \frac{1}{2} O_2 \rightarrow CO$$
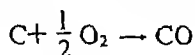
It is a colourless, odourless and a poisonous gas. Carbon monoxide reacts with the haemoglobin in the red blood cells and destroys their capacity to supply oxygen to the body.

Two important industrial fuels, water gas and producer gas, contain carbon monoxide along with hydrogen and nitrogen, respectively. Water gas is obtained by passing steam over hot coke·

$$C + H_2O \rightarrow CO + H_2$$
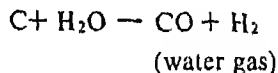
(water gas)

When air is used instead of steam, producer gas is formed:

$$2C + O_2 + 4N_2 \rightarrow 2CO + 4N_2$$
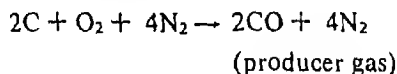
(producer gas)

Carbon monoxide can undergo further combustion forming carbon dioxide and liberating heat. Water gas and producer gas are thus industrially important fuel gases Carbon monoxide is also a powerful reducing agent and reduces many metal oxides to the corresponding metals.

$$2CO + O_2 \rightarrow 2CO_2 + heat$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
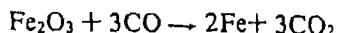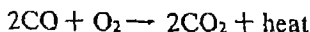
Carbon dioxide is a colourless gas, heavier than air. It is slightly soluble in water. Unlike carbon monoxide, carbon dioxide is not poisonous but it does not support life in animals and humans. It is obtained by the combustion of carbon and other fossil fuels and is present in the atmosphere in small quantities Some of the physical properties of carbon monoxide and carbon dioxide are given in Table 7.1. In the laboratory, carbon dioxide is prepared by the action of acids on carbonates

TABLE 7 1

Some Properties of CO and CO_2

Property	CO	CO_2
m p. (K)	68	216 4 (at 5,2 atm)
b-p (K)	81 5	194.5 (sublimes)
Density (g/L) at 273 K	1 250	1 977
C—O Bond length/pm	112,8	116 3
ΔH_f/kJ mol^{-1}	110,5	−393 5

$$C + O_2 \rightarrow CO_2$$

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$
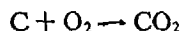
Carbon dioxide dissolves in water to give carbonic acid

$$CO_2 + H_2O \rightarrow H_2CO_3$$
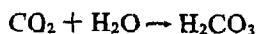
The solubility of CO. in water increases with pressure Soda water and other aerated soft drinks are solutions of carbon dioxide (as well as flavouring and colouring agents) in water under pressure. Carbonic acid is a weak dibasic acid and forms two sets of salts, the hydrogen carbonates HCO_3^- and carbonates CO_3^{2-} In aqueous solution, both carbonates are alkaline due to hydrolysis.

$$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^-$$

$$HCO_3^- + H_2O - OH + H_2CO_3$$
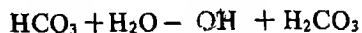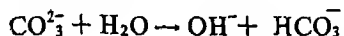
Many carbonates like $Na_2CO_3.10H_2O$ (washing soda), K_2CO_3, $CaCO_3$ and $NaHCO_3$ (baking soda) are commercially important chemicals and are widely used in industry. The manufacture and uses of some of the carbonates are discussed in Unit 14.

Solid carbon dioxide or dry ice is obtained by cooling CO_2 under pressure It passes from the solid state straight to the gaseous state without liquefying (hence dry ice) and is used as a coolant for preserving perishables in the food industry.

While carbonates of many metals are known, only the bicarbonates of the alkali metals exist in the solid state. Bicarbonates of calcium and magnesium are responsible for temporary hardness of water.

7.3.2 Halides

All the four possible tetrahalides of carbon are known (CF_4, CCl_4, CBr_4 and CI_4) In addition, mixed halides like $CFCl_3$, CF_2Cl_2 and CCl_3Br are also known. The halides,

especially those containing both flourine and chlorine are chemically inert non-flammable gases or liquids. Some of these compounds find wide use in industry. Thus, carbon tetrachloride is a common solvent and CF_2Cl_2 is used as a refrigerant.

7.3.3 Carbides

Carbon combines with more electropositive elements than itself when heated to high temperatures to form carbides. Some typical examples are silicon carbide (SiC, also known as carborundum), tungsten carbide (WC) and calcium carbide (CaC_2). Silicon and tungsten carbides are extremely hard materials which find use as abrasives and in cutting and drilling tools. Calcium carbide is the chief source of acetylene gas (C_2H_2) used for welding.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$
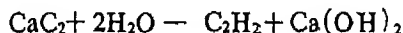
In the early years of chemistry, compounds were classified into two types. Compounds derived form non-living matter like minerals and rocks were 'inorganic compounds' and those obtained from plant and animal sources were 'organic compounds'. The mistaken notion that a 'vital force' present in living systems was essential for the synthesis of organic compounds led to the belief that they could not be synthesised in the laboratory. The rapid development of chemistry in the early years of the nineteenth century however changed the picture. In 1828, Wohler synthesised the hitherto known organic compound urea (present in urine) from the inorganic compound ammonium cyanate.

$$NH_4^+CNO \xrightarrow{\text{heat}} NH_2CONH_2$$
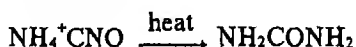
Lavoisier showed by qualitative and quantitative analysis (see Unit 18) of numerous organic compounds that they were made up of relatively few elements and that they all contained carbon. The pioneering work of chemists like Kolbe, Kekule and Bertholet established organic chemistry as the chemistry of carbon compounds, generally containing carbon-carbon bonds. Organic compounds usually contain hydrogen and also oxygen, nitrogen, sulphur, phosphorus and the halogens.

More than five million organic compounds are known. They comprise about 90% of *all* known compounds. Therefore, before we begin to study organic chemistry, we should understand the reason why so many organic compounds are known. As mentioned in the previous paragraph, organic compounds have carbon-carbon bonds. No other element forms bonds with itself so easily. This phenomenon of an atom bonding to itself is known as *catenation*. Carbon-carbon bonds are strong compared to carbon-hydrogen or carbon-oxygen bonds. The silicon-silicon bond,

however, is much weaker than the silicon-oxygen bond, accounting for the abundance of silicon-oxygen bonds (silica and silicates) in nature

A second reason for the abundance of organic compounds is the phenomenon of ISOMERISM. Two compounds are said to be isomers if they have the same molecular formula, but different arrangement of atoms. For example, there are two compounds with the formula C_4H_{10}. Compounds A is known as n-butane and compound B as 2-methylpropane They differ in the way the carbon atoms are bonded and have different properties. For example, A boils at 272 K and B at 261 K A detailed discussion on isomerism is given later in this book

$$CH_3 - CH_2 - CH_2 - CH_3 \qquad\qquad CH_3 - CH - CH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
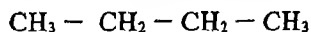
$$\qquad\quad A \qquad\qquad\qquad\qquad\qquad\qquad B$$

Generally, organic compounds are studied separately from inorganic compounds. First, and probably the most important reason for doing this, is the existence of a very large number of organic compounds. A second factor is that while most reactions in inorganic chemistry are ionic and occur quite rapidly, most organic reactions involve covalent bonds and are relatively slow. Although the number of known organic compounds is large, the types of reactions they undergo are easy to systematise and understand. Based on functional groups, organic compounds can be classified into families. (For the definition of functional groups, see Sec. 7.5 2). The chemistry of two compounds having the same functional group is usually very similar. This simplifies the study of organic chemitry.

Organic compounds play an important part in our daily lives. All living systems obtain their energy from organic compounds like carbohydrates (sugars) and fats and grow using amino acids and proteins (again organic). They transmit genetic information from one generation to the next via nucleic acids (also organic) The clothes we wear, be they of natural fibres like cotton, wool or silk or synthetic material like polyester are organic compounds Most of the drugs and pharmaceuticals are also organic compounds. In agriculture too, organic chemistry is well represented. Fertilizers like urea, pesticides like DDT, malathion and gammaxene, and plant growth regulators are all organic chemicals. Among our various energy sources, fossil fuels like coal, lignite, petroleum and natural gas are of organic origin. Many commonly used polymers (natural and synthetic—like wood, rubber, paper and plastics are again organic compounds.

7.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming them has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) Nomenclature All the

names used in this book follow the IUPAC system. However, the more common names are still widely used by chemists and these are given in parenthesis.

7.5.1 Hydrocarbons

Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The systematic IUPAC name for such a compound is an alkane. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those which contain at least one carbon-carbon double or triple bond. Alkenes, alkynes and arenes are all unsaturated hydrocarbons. Hydrocarbons are classified into three types depending on their structure (arrangement of carbon atoms).

1. Straight chain compounds
2. Branched chain compounds
3. Cyclic compounds

Nomenclature of alkanes: Straight chain compounds: As the name itself implies, these compounds are made up of straight chains of carbon atoms. The names of such compounds are made up of straight chains of carbon atoms. The names of such compounds end with 'ane' and carry a prefix indicating the number of carbon atom present (except from CH_4 to C_4H_{10}, where the prefixes are derived from older, trivial names) A list of names of alkanes containing carbons 1-10 is given below:

1.	CH_4	methane	6.	C_6H_{14}	hexane
2.	C_2H_6	ethane	7.	C_7H_{16}	heptane
3.	C_3H_8	propane	8.	C_8H_{18}	octane
4.	C_4H_{10}	butane	9.	C_9H_{20}	nonane
5.	C_5H_{12}	pentane	10.	$C_{10}H_{22}$	decane

The general molecular formula for an alkane can thus be written as C_nH_{2n+2}. It is seen that each compound in the above list can be obtained from the previous compound by adding a CH_2 unit A series of compounds differing by a CH_2 unit is called a HOMOLOGOUS SERIES and its members display a gradation in physical properties and similarity in chemical properties.

A compound can be represented by its molecular formula, structural formula and graphic or displayed formula. Thus in the case of propane, we have the following.

$$C_3H_8 \qquad CH_3-CH_2-CH_3 \qquad$$

$$
\begin{array}{ccc}
H & H & H \\
| & | & | \\
H-C-&C-&C-H \\
| & | & | \\
H & H & H
\end{array}
$$

Molecular formula   Structural formula   Graphic formula
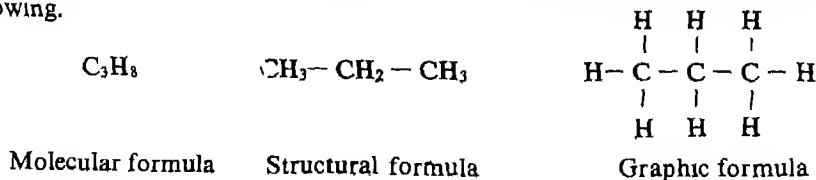
Structural formula is the one used most often.

Branched Chain Compounds: In branched chain compounds, all the carbon atoms are not present in a linear sequence. Some of them are attached to the chain at one or more points, like, for example, in the compound given below.

$$CH_3- CH - CH_2 - CH_2 - CH_2 - CH - CH_2 - CH_2 - CH_3$$
$$\qquad | \qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad CH_3 \qquad\qquad\qquad\qquad\qquad CH_2 - CH_3$$
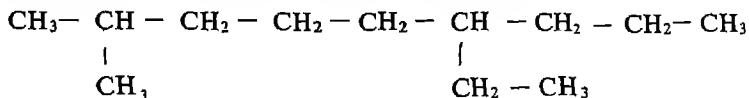
While these compounds are still alkanes with the general molecular formula C_nH_{2n+2}, the presence of branching prevents direct naming of them, To overcome this difficulty, groups of atoms called alkyl groups are used. An alkyl group is obtained from a straight chain hydrocarbon by removing a hydrogen atom from a carbon. The position of the hydrogen atom removed is indicated by giving it the lowest possible number from the chain terminus. Thus, CH_4 becomes CH_3- and is called methyl group. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding straight chain alkane. Some examples are listed below.

Hydrocarbon		**Alkyl group**	
Molecular formula	*Name*	*Molecular formula*	*Name*
CH_4	methane	CH_3-	methyl
C_2H_6	ethane	CH_3CH_2-	ethyl
C_4H_{10}	butane	$CH_3CH_2CH_2CH_2$-	l-butyl
$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_2$-	l-decyl
		$CH_3(CH_2)_5CHCH_2CH_2CH_3$	4-decyl and not 6-decyl

A branched chain alkane is named using the following sequence.

1. First, the longest straight carbon chain present in the molecule is identified. In the example given earlier, the longest chain has nine carbons.

```
1  2  3  4  5  6  7  8  9      1  2  3  4  5  6
C—C—C—C—C—C—C—C—C          C—C—C—C—C—C—C—C—C
   |           |                  |           |
   C           C—C                C           C—C
                                              7  8
```
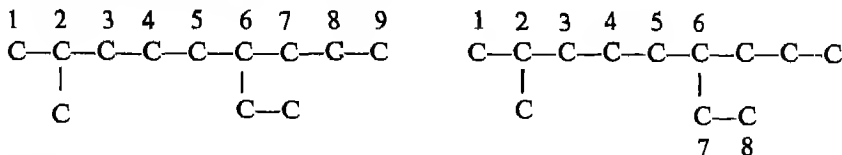
2. The carbon atoms on this chain are numbered to identify the position of the alkyl group in the branch (or side chain) The numbering is done in such a way

that the substituted carbon atoms have the lowest possible numbers. Thus, the numbering in the illustrated example should be from left to right (substituted carbon atoms 2 and 6) and not from right to left (substituted carbon atoms 4 and 8).

```
1   2   3   4   5   6   7   8   9          9   8   7   6   5   4   3   2   1
C—C—C—C—C—C—C—C—C                    C—C—C—C—C—C—C—C—C
    |               |                             |               |
    C               C—C                           C               C—C
```
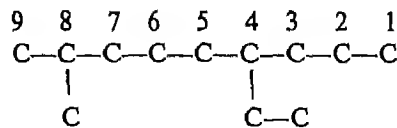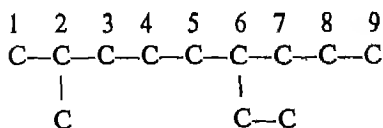
3. The substituent alkyl groups are then prefixed to the name of the parent alkane, the position of the substituents being indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. The full name for the example given above is 6-ethyl-2-methylnonane Note that the numbers are separated from the groups by hyphens and that there is no break between methyl and nonane.

4. If two or more identical groups are present as in the examples shown below, then the numbers are separated by commas,

$$CH_3 — CH — CH_2 — CH — CH_3$$
$$\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad CH_3 \qquad\qquad CH_3$$

2,4-dimethylpentane

$$\qquad\qquad\quad CH_3$$
$$\qquad\qquad\quad |$$
$$CH_3 — C — CH_2 — CH — CH_3$$
$$\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad CH_3 \qquad\qquad CH_3$$
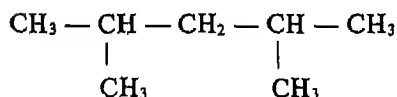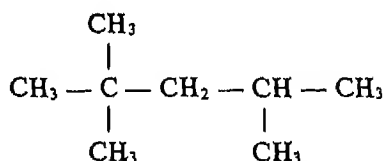
2,2,4-trimethylpentane

Cyclic Compounds: A cyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given in the previous section are applied. Thus, for example, the structures shown below are cyclopentane and 1-methyl-3-propylcyclohexane, respectively.

$$CH_3$$
$$|$$
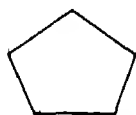
cyclopentane   1-methyl-3-propylcyclohexane

$$CH_2 CH_2 CH_3$$
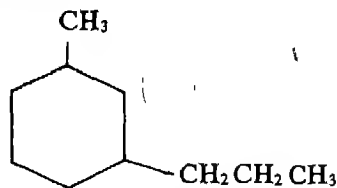
7.5.2 Functional Groups

The nomenclature of organic compounds is considerably simplified by what are called functional groups. A functional group is an atom or group of atoms bonded together in a unique fashion and having characteristic chemical properties Thus, for example, an alcohol functional group is represented by $-O-H$ and a carboxylic acid by $-\underset{\underset{O}{\|}}{C}-O-H$ All compounds having the same functional group will undergo similar reactions Illustratively, the alcohols CH_3 OH, CH_3 CH_2 OH and $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ all liberate hydrogen on reaction with sodium metal

$$2R-OH + 2Na \longrightarrow 2RONa + H_2$$
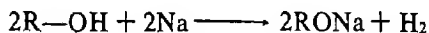
where $\quad R = CH_3 -$ or $CH_3CH_2 -$ or $CH_3 - CH-CH_3$

This similarity in chemical behaviour is due to the fact that carbon-carbon single bonds and carbon-hydrogen bonds are quite strong and do not break easily, whereas an $-O-H$ bond is weaker and hence more reactive Any molelcule having the same functional group will behave in a similar way, no matter what the rest of the molecule may be Exceptions are known, of course, if the moelcule is very large or has two more functional groups close to one another The presence of functional groups enables the systematisation of organic compounds into different classes Therefore, before naming an organic compound, it is necessary to first name the different classes of functional groups Table 7 2 lists some of the more important functional groups

Naming an Organic Compound· The systematic name of an organic compound can be easily obtained using the above Table 7.2 To do this, the folowing sequential procedure is adopted.

Step 1   The functional group present is identified This enables the appropriate suffix or prefix to be chosen

Step 2   The longest chain *containing the functional group* is identified, fixing the name of the corresponding saturated hydrocarbon.

Step 3   Following the principle of assigning the lowest possible number to the functional group, the chain is numbered.

Step 4.   The name is then arrived at

TABLE 7.2
Some Important Functional Groups

Class of Compounds (functional group)	Structure of the functional group	IUPAC suffix(s)* or prefix(p)	Example
Alkane	—	—ane(s)	Butane $CH_3CH_2CH_2CH_3$
Alkene	C=C	—ene(s)	1—Butene $CH_2=CHCH_2CH_3$
Alkyne	C≡C	—yne(s)	1-Butyne $CH\equiv CCH_2CH_3$
Arene	———	—	Benzene =
Alcohol	—OH	ol(s)	2-Butanol $CH_3CHCH_2CH_3$ $\overset{\mid}{O}H$
Ether	$-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	——	Ethoxyethane $CH_3CH_2OCH_2CH_3$ or Diethyl ether
Aldehyde	$-\underset{\overset{\mid}{H}}{C}=O$	—al(s)	1—Butanal $CH_3CH_2CH_2CHO$
Ketone	$-\underset{\mid}{C}=O$	—one (s)	2-Butanone $CH_3\overset{\mid\mid}{\underset{O}{C}}CH_2CH_3$
Halide	—X (X=F,Cl,Br,I)	Halogeno(p) or —yl halide(s)	1—Bromobutane $CH_3(CH_2)_3Br$ or n—Butyl bromide
Nitro	—NO₂	Nitro—(p)	1-Nitrobutane $CH_3(CH_2)_3NO_2$
Amine	—NH₂,—NH,—N—	Amino—(p) or —amine(s)	2—Aminobutane $CH_3CHCH_2CH_3$ or 2 — Butaneamine NH_2
Carboxylic acid	$-\underset{\overset{\mid\mid}{O}}{C}-OH$	—oic acid(s)	Butanoic acid $CH_3CH_2CH_2COOH$
Carboxylate ion	$-\underset{\overset{\mid\mid}{O}}{C}-O$	—oate(s)	Sodium $CH_3CH_2CH_2COO^-Na^+$ butanoate
Acid anhydride	$-\underset{\overset{\mid\mid}{O}}{C}-O-\underset{\overset{\mid\mid}{O}}{C}-$	— oic anhydride(s)	Butanoic $CH_3 CH_2 CH_2 C=O$ anhydride $CH_3CH_2CH_2C=O$
Amide	$-\underset{\overset{\mid\mid}{O}}{C}-NH_2,-\underset{\overset{\mid\mid}{O}}{C}-NHR,-\underset{\overset{\mid\mid}{O}}{C}NR_2$ —amide(s)		Butanamide $CH_3CH_2CH_2CNH_2$ $\overset{\mid\mid}{O}$
Acyl halide	$\underset{\overset{\mid\mid}{O}}{C}-X$	—oyl halide(s)	Butanoyl $CH_3CH_2CH_2CCl$ chloride $\overset{\mid\mid}{O}$

* The suffix or prefix is attached to the corresponding parent saturated hydrocarbon.

Some typical examples are illustrated below.

Example 7 1

$$\overset{1}{C}H_3\!-\!\overset{2}{C}H_2\!-\!\overset{3}{C}H\!-\!\overset{4}{C}H_2\!-\!\overset{5}{C}H_2\!-\!\overset{6}{C}H\!-\!\overset{7}{C}H_2\,\overset{8}{C}H_3$$

$$\underset{\quad\;\;OH}{|}\qquad\qquad\underset{\quad\;\;CH_3}{|}$$
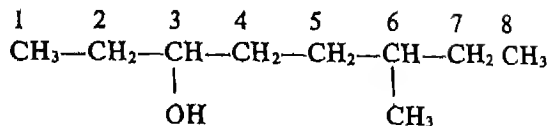
Solution

1. The functional group present is an alcohol Hence the suffix is -ol.
2. The longest chain containing —OH has eight carbons. Therefore the corresponding saturated hydrocarbon is octane.
3. The —OH is on carbon 3. In addition, a methyl group is attached to carbon 6.
4. The systematic name is therefore 6- methyl-3- octanol.

Example 7 2

$$\overset{6}{C}H_3\;\overset{5}{C}H_2\;\overset{4}{C}H_2\;\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}OOH$$
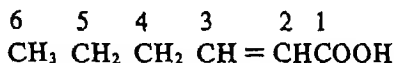
Solution

1. Here two functional groups are present, namely, an alkene and a carboxylic acid. The suffix should therefore indicate both. This is done by combining – ene and – oic acid into – enoic acid.
2. The parent hydrocarbon is hexane as six carbons are in the chain.
3. The double bond is present in the 2-position.
4. The complete name is 2-hexenoic acid.

Deriving the Structure from the Name: In a similar manner, for a given systematic name, the corresponding structure can be drawn as shown in the following examples.

Example 7 3

Solution   5-Chloro–2- pentanone.

1. A five carbon chain is present as indicated by penta.
   C — C — C — C — C
2. The functional groups present are a ketone at the second carbon and a chlorine at the fifth carbon.

$$C\!-\!\underset{\underset{O}{\|}}{C}\!-\!C\!-\!C\!-\!C\!-\!Cl$$
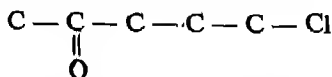
3. Filling in the hydrogens, we get

$$CH_3\!-\!\underset{\underset{O}{\|}}{C}\!-\!CH_2\!-\!CH_2\!-\!\overset{.}{C}H_2\!-\!Cl$$
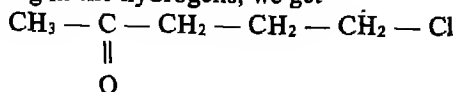
Example 7.4

3-Nitrocyclohexene

Solution

1. A six-membered ring is present as indicated by cyclohexene Further, the ending –ene denotes the presence of a double bond.
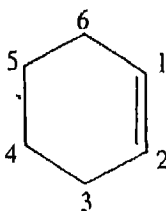
The numbering is as shown above.

2. The prefix 3-nitro means that a nitro group is present on the third carbon.

3. The complete structural formula is
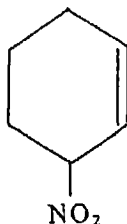
7.6 SOME COMMON ORGANIC COMPOUNDS

In this section some common organic compounds are mentioned along with their principal uses. Illustrative examples have been chosen from the different functional groups listed in Table 7.2. The details of the chemistry of these compounds will be discussed in later Units

Alkanes Petroleum and natural gas are largely mixtures of different alkanes. On refining, they give liquefied petroleum gas (LPG), petrol, kerosene, diesel, furnace oil and wax, in the order of increasing carbon content The uses of these compounds are well known.

Alkenes: The lower alkenes (C_2 to C_4 or C_5) are obtained as products of petroleum refining. Alkenes are primarily used to prepare different polymers like polyethylene (from ethene), polypropylene (from propene), synthetic rubber (from 1,3—butadiene) and also other compounds like alcohols, aldehydes and ketones on a large scale.

Alkynes: The most important alkyne is ethyne (acetylene) which is used for welding purposes

Arenes. Arenes arc also known as aromatics. Simple arenes like benzene, toluene and xylene are used to manufacture synthetic detergents, synthetic fibres and explosives (e.g. TNT) Naphthalene is a constituent of mothballs and many compounds obtained from naphthalene and anthracene are used to prepare artificial dyes for textiles. The chief sources of arenes are petroleum and coal

Alcohols Methanol and ethanol are the two most important alcohols. While methanol is largely manufactured from petroleum feedstock, ethanol is obtained from ethene or by fermentation of sugar and starch. Both have many uses in industry and ethanol has been suggested as a fuel from a renewable resource like sugarcane Compounds derived from 2—ethylhexanol are used as softeners in plastics. 1,2-ethanediol (ethylene glycol) is a raw material for dacron (synthetic fibre) manufacture and 1,2,3-propanetriol (glycerol) is used in confectionery and cosmetics

Aldehydes and Ketones; Methanal (formaldehyde) and ethanal (acetaldehyde) are important raw materials, used widely in the plastic industry. In addition, methanal is a good disinfectant and preservative (formalin) Propanone (acetone) and 2-butanone (methyl ethyl ketone or MEK) are important laboratory and industrial solvents and cyclohexanone is an intermediate in the manufacture of nylon

Halides· Chlorinated compounds of methane, ethane and ethene are all widely used solvents like dichloromethane, tricholoromethane (chloroform), tetrachloromethane (carbon tetrachloride), 1,2-dichloroethane, trichloroethene and tetrachloroethene 1,2-dibromoethane is used as a fumigant against insects in food storage godowns The well known insecticide DDT contains chlorine 1-bromo-1-chloro-2,2,2-trifluoroethane is a commonly used anaesthetic Freon or dichlorodifluoromethane is employed in refrigeration and cooling systems

Acids; The simple acids like methanoic acid (formic acid) and ethanoic acid (acetic acid) are present in ants and vinegar, respectively. Ethanoic acid is used to produce rayon plastics and paints Sodium and potassium salts of oleic acid etc hexadecanoic (palmitic) and octadecanoic (stearic) acids are used as soaps Vegetable cooking oils and vanaspati are also derived from such long chain acids

Nitro Compounds Nitromethane, nitroethane and nitrobenzene are useful industrial solvents Many nitro compounds like nitroglycerol, nitrocellulose and trinitrotoluene (TNT) are used as explosives

Amines; Compounds containing both amine and carboxylic acid functional groups are called amino acids Many amino acids are constituents of proteins which are the basic building blocks of living things Amines are also used to manufacture nylon Aromatic amines are important intermediates in the dyestuff industry

EXERCISES

7.1 What is allotropy? Name some elements which exhibit allotropy.

7.2 Explain the differences in the properties of diamond and graphite based upon their structures.

7.3 Give equations for the following:
    (i) Preparation of carbon dioxide
    (ii) Basic properties of sodium carbonate solution
    (iii) Formation of acetylene.

7.4 What is dry ice? Why is it so called?

7 5 What are isomers?

7.6 What is a functional group?

7.7 Name the different types of hydrocarbons.

7.8 In what way does an alkane differ from the other hydrocarbons?

7 9 Give systematic IUPAC names for the following compounds.

(i) $CH_3 CHCH_2 CH_2 CHCH_2 CH_3$
           | |
           CH_3 CH_3

(ii)

(iii) $CH_3 CH_2 CCH_2 CH_2 CH_3$ with Cl above and Br below the central C

(iv) $CH_3CH_2 CHCH_2 CHO$
             |
           CH_3

(v) $ICH_2 CH_2 CH_2 CO_2 H$

$$
\begin{array}{c}
\quad\quad\ \ O \\
\quad\quad\ \ \parallel
\end{array}
$$

(vi) CH₃ CH CCH₂ CH₂ CH₂ Cl
            |
            CH₃
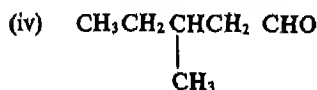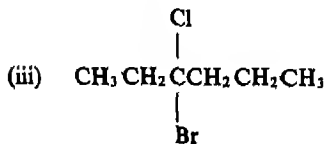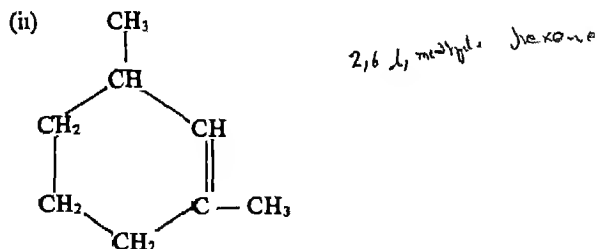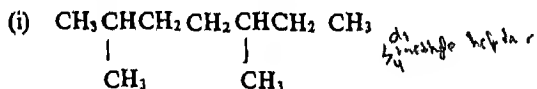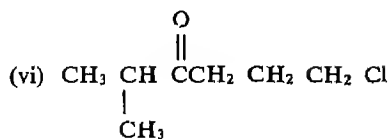
7.10   Draw the structures of the following compounds

    (i) 3-Hexenoic acid
    (ii) 2-Chloro-2-methylbutanol
    (iii) 5,5-Diethyl-3-nonanol
    (iv) 1-Bromo-3-chlorocyclohexene
    (v) 4-Nitro-1-pentyne
    (vi) 1,3-Diaminopropane

7 11   Draw the structure of the functional group corresponding to.

    (a) Aldehyde
    (b) Nitro
    (c) Carboxylic acid
    (d) Ether

UNIT 8

ENERGETICS

*Heat and cold are Nature's two
hands with which she cheerfully
works*

OBJECTIVES

In this Unit, we shall learn

*. the nature of energy changes in chemical reactions;

* the distinction between exothermic and endothermic reactions;

* to express energy changes in terms of the enthalpy concept,

* to calculate bond energy with the help of enthalpy changes;

* the different sources of energy and their importance in daily life;

* to predict the directions of a reaction using the entropy and the free
energy concepts.

EVERY CHEMICAL REACTION involves rearrange-
ment of atoms In the earlier Unit we have learnt
to keep account of the changes in terms of masses
of products formed from reactants. In this Unit we
shall pay attention to the energy changes that must
accompany any chemical change since chemical
bonds are broken and reformed. In our chemical
arithmetic we shall account for energy changes
also.

Fig. 8.3 (a)

Fig. 8.3 (b)

We will now define some basic terms which
are used in the discussion of energetics ·

A SYSTEM is defined as that part of the Universe
which is under investigation while everything else is
defined as making up the SURROUNDINGS. For
example, if we are interested in investigating a
reaction, then the reaction mixture (i.e., reactants
and products) is our system and all the rest (i.e.,
the reaction vessel, the outside room, etc) are the
surroundings.
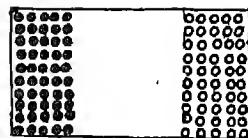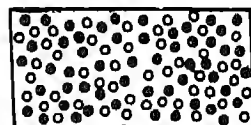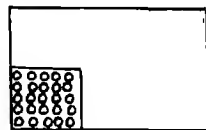
Fig 8.4

Every system has a definite amount of energy. A system can lose energy to the
surroundings, or gain energy from the surroundings, in a variety of ways. For
example, if a system is at a higher temperature, then energy is lost to the sur-
roundings causing a fall in the temperature of the system and a rise in the tempera-
ture of the surroundings. The energy transfer goes on until the system and the
surroundings attain the SAME temperature The energy exchanged between a system
and the surroundings when their tempeartures are different is commonly known as
HEAT. It is important to realise (i) that heat is not a substance, and (ii) that a system
does not have a definite amount of heat (but as stated earlier, it has a definite
amount of energy). What do we mean when we use terms like 'heat is flowing'? All
that we mean is that energy is being exchanged because of a difference in tempera-
tures Another mode of energy transfer is WORK For example, if a gas, enclosed in
a cylinder with a piston, has a higher pressure, the piston will be pushed up until the
pressure inside and outside become equal. The energy transfer that takes place in
this case is called work. If the system loses energy, one says that work is done by the
system; if the system gains energy, one says that work is done on the system. It
should be noted that work, like heat, is also not a property of the system, i.e., a
system does not have a difinite amount of work. To summarise, the amount of
energy in a system is fixed and it remains so if there is no interaction with the

surroundings, i.e., if the system is isolated*. If the system is not isolated, energy can be transferred in or out of the system. The energy transfer because of the difference in temperature is referred to as heat and that due to difference in pressure is one type of work.

8.1   ENERGY CHANGES DURING A CHEMICAL REACTION

The most common sources of energy are the fuels: kerosene, coal, charcoal and wood. The molecules present in these substances react with the oxygen in air to provide heat, light and very often smoke and this reaction is termed as 'combustion'. Combustion is an example of a chemical reaction from which we derive energy for our benefit. Fuels provide the energy for all activities of life Other examples which can be only tested are as follows:

a) You must also have observed that specially roasted marbles or sea-shells (called quick lime, or *chuna* in Hindi) are mixed with water to prepare whitewash. When some water is added on a pile of quicklime a considerable amount of heat is generated.

b) In a test tube containing granulated zinc, when you add a few cm^3 of dilute hydrochloric acid and feel the test tube, you will find that a gas evolves (what gas?) and a chemical reaction takes place.

c) When you light a matchstick by rubbing it on the side of a match-box, a chemical reaction takes place. Light, heat and fumes emerge.

In all the cases we have considered until now a chemical reaction leads to energy being released to the surroundings. Can we have a situation when chemical reactions result in the absorption of energy from the surroundings?

d) In a test tube containing 10 cm^3 of water, add 1g of solid ammonium chloride and stir. You will find a decrease in the temperature of the water when the salt is dissolved

e) A similar experiment when repeated with 1g of solid sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$, is found to lead to a decrease in temperature.

f) When hydrated barium hydroxide powder (say, 1g) is mixed with ammonium chloride (say, 0.1g), in a water glass a reaction takes place and the temperature of the system falls rapidly.

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl\ (s) \longrightarrow BaCl_2 \cdot 2H_2O\ (s) + 2NH_3\ (aq) + 8\ H_2O\ (l)$$

In certain reactions, energy is released leading to an increase in temperature; in certain other cases, energy is abosrbed leading to a fall in temperature. It is not

---

* A cup of coffee in a lhermos flask is a simple example of an isolated system The hol coffee stays hot because the sytem is unable to lose energy lo the surroundings The same cup of coffee outside the flask cools down to the room temperature because heat (i.e , energy) flows from the coffee to the surroundings due lo difference in temperatures.

surprising that energy changes accompany a chemical reaction, since during a chemical reaction bonds between atoms in the reactant molecules are rearranged to form product molecules. *Energy is needed to break chemical bonds and energy is released when bonds are formed.* Since the bond energy varies from one bond to another, there is bound to be an energy change when products are formed from reactants.

The energy change that accompanies a chemical reaction need not necessarily be expressed in the form of evolution or absorption of heat. Energy can be released or absorbed in other forms such as light, electricity, mechanical energy (e.g., sound). Electrical energy obtained from chemical reactions in batteries runs your transistor radio, torch or watch. Heavy duty batteries start your car, lorry, bus or tractor. In electrolysis of acidified water, energy in the form of electricity is absorbed to split water into its elements, hydrogen and oxygen (Unit 10). Diwali crackers give out energy in the form of light and mechanical energy (sound is produced and the explosion leads to small parts of the crackers flying off with a large amount of kinetic energy). In the 'pop' test for hydrogen, sound energy is released. In cars, trucks, tractors and buses, heat energy accompanying the reaction of petrol or diesel with oxygen from the air, is converted to mechanical energy (kinetic energy of the moving object).

One of the most important reactions that occurs in nature, and on which sustenance of life depends, is photosynthesis. In this process, green plants convert carbon dioxide and water into starch and oxygen. Energy has to be supplied for this chemical change and it is provided by the energy of sunlight.
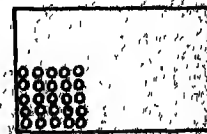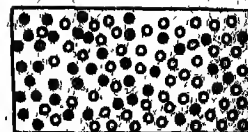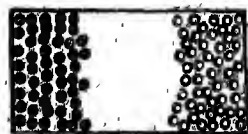
8.2 INTERNAL ENERGY AND ENTHALPY

8.2.1 Internal Energy

A fixed quantity of any substance, under a given set of conditions, has got a definite amount of energy associated with it. This amount is different for different substances. The energy stored in a compound is called its internal energy and it is denoted by the symbol E. When a chemical reaction occurs, the internal energy of the system before the reaction is generally different from the internal energy after the reaction. This is because the internal energy of the reactants is almost always different from that of the products. If a reaction is carried out in such a manner that there is no change in temperature and the system does not do any work nor has work done on

it then, the internal energy change (ΔE) of the reaction is equal to the energy exchanged with the surroundings (here 'Δ' is pronounced as delta and stands for 'd' in Greek indicating difference). This is a consequence of the law of conservation of energy which we discuss later. In usual practice, the energy exchange can be measured in the form of heat exchanged with the surroundings and the work can be associated with a change of volume against pressure. The change in internal energy (ΔE) in a chemical reaction is therefore obtained by carrying out the reactions *at constant temperature and constant volume* and measuring the heat exchanged with the surroundings. Since the volume is constant, there is no work done. All the energy exchanged with surroundings has to arise from changes in internal energy.

8.2.2 Enthalpy and Enthalpy changes

It is more convenient to carry out reactions in the laboratory in open containers (open beaker, test tubes, etc.). A system open to the atmosphere is obviously at atmospheric pressure. When a chemical reaction takes place in contact with the atmosphere, the volume may change but the pressure continues to be equal to the atmospheric pressure. Since atmospheric pressure is practically constant, chemical changes in open containers can be considered as taking place at cosntant pressure but not at constant volume.

The amount of heat exchanged with the surroundings for a reaction at constant pressure and temperature differs from that exchanged at constant volume and temperature. The reason is easy to understand. At constant pressure, the volume of the reacting system usually changes. If the volume increases, the system has to expand against the atmospheric pressure and energy in needed for this task. The amount of heat exchanged at constant pressure would therefore be less than the amount exchanged at constant volume. This is because, a part of the energy has been utilised for the expansion of the system. If however, the system contracts at constant pressure work is done on the system. The amount of heat exchanged at constant pressure in this case is therefore greater than that exchanged at constant volume.

These considerations show that energy changes in a reaction at constant pressure and temperature are not due to changes in the internal energy alone but they also include energy contribution due to expansion or contraction against the atmosphere. To handle this situation, another property called ENTHALPY* denoted by the symbol

---

* Instead of enthalpy many chemists prefer to use the term heat content! Enthalpy changes in various processes, like combustion, fusion and neutralisation are thus also called heat of combustion, heat of fusion and heat of neutralisation respectively.

Enthalpy of an element or a compound, depends upon the temperature and pressure. If we wish to compare ΔH values, the conditions under which they have been measured must be identical . On normal course, while indicating enthalpy changes we take the STANDARD STATE of a substance. The standard state of substance is the state in which the substance is stable at 1 atm pressure and 298K In this book, the data used for enthalpy changes (ΔH) are given in the standard state.

H is associated with every substance. The energy change at constant pressure and temperature is called the enthalpy change (denoted by the symbol ΔH), it is equal to the amount of heat exchanged with the surroundings at constant pressure and constant temperature. (In normal practice, we insulate the system from its surroundings and allow the heat of reaction to change the temperature of the system. We then calculate how much heat would have to be put into or taken from the system to bring it back to its initial temperature. This amount of heat is the enthalpy change.)
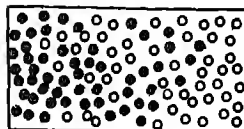
In dealing with energy changes, it is important to remember that energy may change from one form to another, but the total energy of system and its surroundings remains constant. This guiding principle which is known as the LAW OF CONSERVATION OF ENERGY can also be stated in another way According to this law,

energy is neither created nor destroyed. This holds in chemical reaction as well. Energy may be absorbed or released in chemical reaction, but the total energy of the reacting system and its surroundings remains constant.
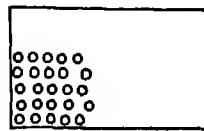
A chemical reaction involves reactant(s) and product(s). A given set of reactants has a definite total enthalpy, $H_{reactants}$. The corresponding set of products also has a definite total enthalpy, $H_{products}$. The difference between these enthalpies, ΔH, is HEAT OF REACTION.

$$\Delta H = H_{products} - H_{reactants}$$

When total enthalpy of the products, $H_{products}$ is greater than the total enthalpy of the reactants, $H_{reactants}$, ΔH is positive and heat is absorbed in the reaction, the reaction will be ENDOTHERMIC Combination of H_2 with I_2 to give HI is an endothermic reaction (Fig. 8 la)
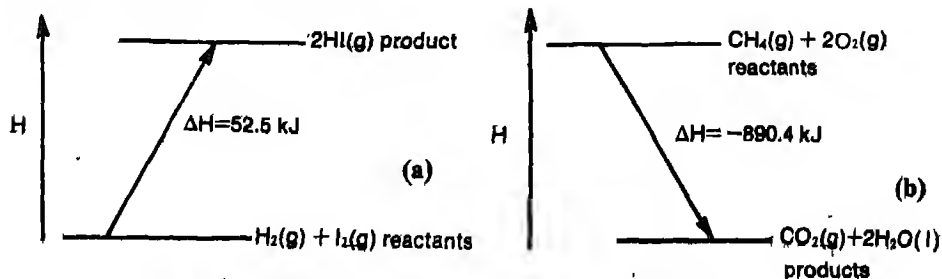
Fig. 8.1 *Enthalpy changes in endothermic and exothermic reaction.*

$$H_2(g) + I_2 (g) \longrightarrow 2HI (g); \Delta H = 52.2 \text{ kJ}$$

Here, 52 2 kJ of heat are absorbed for every mol of H_2 and I_2 used up and for every 2 mol of HI produced in the reaction, at constant pressure

When total enthalpy of the products is less than that of the reactants, ΔH is negative and heat is evolved. The reaction will be EXOTHERMIC. Combination of methane with oxygen is an exothermic process (Fig 8.1b)

$$CH_4 (g) + 2O_2(g) \longrightarrow CO_2 (g) + 2H_2O (l); \Delta H = -890\ 4 \text{ kJ}$$
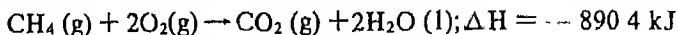
Here 890.4 kJ of heat is evolved for every mol of methane gas burnt.

Let us take a few more such reactions.

$$C_4H_{10} (g) + \frac{13}{2} O_2 (g) \longrightarrow 4 CO_2 (g) + 5H_2O (l); \Delta H = -2876 \text{ kJ}$$

$$SnO_2(s) + 2C(s) \longrightarrow Sn(s) + 2CO (g); \Delta H = +360 \text{ kJ}$$

$$H^+(aq) + OH^- (aq) \longrightarrow H_2O (l); \Delta H = -57\ 1 \text{ kJ}$$
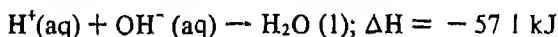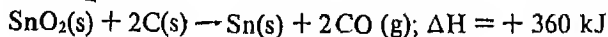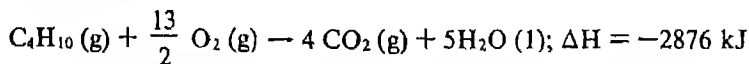
ΔH refers to the chemical equation written along with it, unless otherwise specified

In writing a thermochemical equation,

$$C_4H_{10} (g) + \frac{13}{2}O_2 (g) \longrightarrow 4CO_2 (g) + 5H_2O (g) + 2658 \text{ kJ}$$
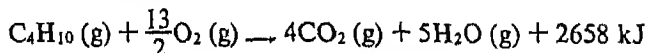
We do not state the conditions under which the energy is released. Therefore chemists prefer to write the above equation as

$$C_4H_{10}(g) + \frac{13}{2}O_2 (g) \longrightarrow 4 CO_2(g) + 5H_2O(g); \Delta H_{298} = -2658 \text{ kJ}$$
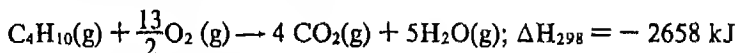
indicating that the energy is released in the form of heat at constant temperature (298 K) and constant pressure (1 atmosphere). (One can also write the thermo-chemical equation without indicating ΔH separately and we have followed this method for the sake of simplicity and convenience in some of the equations and in the exercises

8.2.3   Origin of Enthalpy Change in a Reaction

Since in a chemical reaction bonds are broken and reformed, we should be able to associate the enthalpy of reactions with the energy changes required to break bonds of the reactants and make new bonds to form products. It is simpler to consider gaseous reactions. In solutions the solvent itself interacts with the reactants and the products and the situation is very complicated. In solids, neighbour-neighbour interactions have to be accounted for. We shall, therefore, consider only elementary reactions in the gas phase to get a feel of the origin of the enthalpy of reactions.

In the gas phase, the enthalpy change of a reaction = (energy required to break the bonds in the molecules of the reactants) — (energy released when bonds in the molecules of the product are formed) at constant pressure.

In the case of formation of HCl (g) from H_2 (g) and Cl_2 (g), $\Delta H = -185$ kJ mol^{-1} of H_2 and Cl_2. This heat of reaction should be the difference between the energy required to break the bonds between H_2 and Cl_2 and the energy released when two molecules of HCl (i e., bonds between H and Cl) are formed.

$$H-H \xrightarrow[\text{breaking bond, } \Delta H = +437 \text{ kJ}]{\text{energy absorbed in}} \quad H + H$$

$$+ \qquad +$$

$$Cl-Cl \xrightarrow[\text{breaking bond, } \Delta H = +244 \text{ kJ}]{\text{energy absorbed in}} \quad Cl + Cl$$

bond formed, energy released $\Delta H = -433$ kJ per mole of HCl formed

HCl   HCl
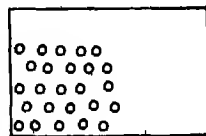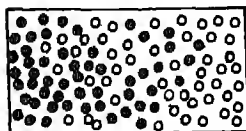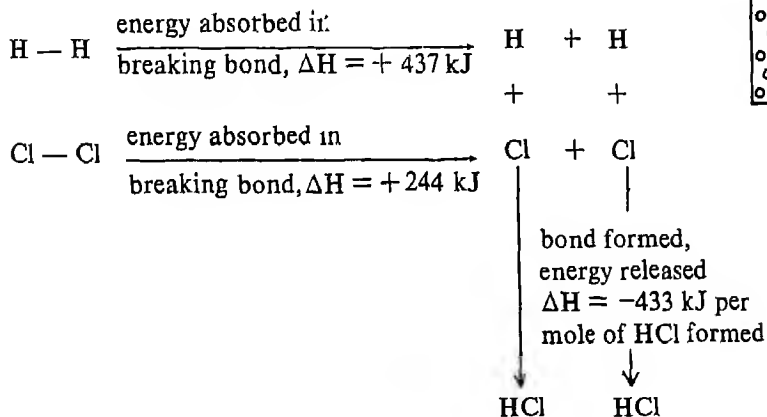
Thus for the reaction,

$$H_2 (g) + Cl_2 (g) \rightarrow 2HCl (g)$$
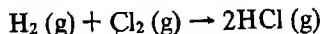
Enthalpy change,

$$\Delta H = (437 + 244) - (2 \times 433)$$
$$= -185 \text{ kJ}$$

8.2.4 Hess's Law of Constant Heat Summation

A consequence of the law of conservation of energy is that the enthalpy of a substance in a particular state is independent of the method we utilised to make that substance in that state. Our definition of the enthalpy change in a reaction as the difference between the enthalpies of products and the enthalpies of reactants is based on the law of conservation of energy.

Let us take oxidation (burning) of carbon to produce CO_2

CONVENTIONS FOR WRITING THE THERMOCHEMICAL EQUATIONS

(i) For exothermic reactions, ΔH is negative and for endothermic reactions, ΔH is positive.

(ii) Unless otherwise mentioned, ΔH values are given for *Standard State* of a substance, i.e., when reactions occur at 298K and standard atmospheric pressure.

(iii) The coefficients of the substances of the chemical equations indicate the number of moles of each substance involved in the reaction (fraction may be used), and the ΔH values given correspond to these quantities of materials.

(iv) For indicating physical state of each substance in a chemical equation, designation such as (g), (s), (l) and (aq) are given along with the chemical formulas of reactants and products.

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \Delta H = -286 \text{ kJ}$$
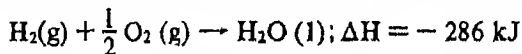
Here 1 mol of hydrogen gas reacts with $\frac{1}{2}$ mol of oxygen gas to produce 1 mol of liquid water. But if 1 mol of water vapour is produced instead of 1 mol of liquid water, the value of ΔH will be different.

$$H_2(g) + \frac{1}{2} O_2 \longrightarrow H_2O(g); \Delta H = -242 \text{ kJ}$$
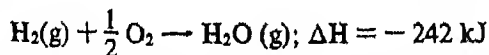
(v) In case the coefficients in the chemical equation are multiplied or divided by a factor, the ΔH value must also be multiplied or divided by the same factor. For example in equation,

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g); \Delta H = -242 \text{ kJ}$$
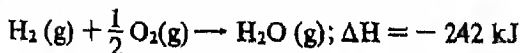
if coefficients are multiplied by 2, we would write the equation

$$2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g); \Delta H = 2 \times (-242) = -484 \text{ kJ}$$
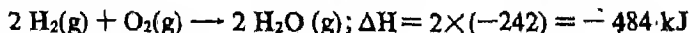
(vi) When a chemical equation is reversed, the sign but not the magnitude of the ΔH value is changed. In other words, a reaction that is endothermic in one direction will be exothermic in the reverse direction. For example,

$$N_2(g) + O_2(g) \longrightarrow 2NO(g); \Delta H = 180.5 \text{ kJ (endothermic)}$$

$$2NO(g) \longrightarrow N_2(g) + O_2(g); \Delta H = -180.5 \text{ kJ (exothermic)}$$

C (graphite) + O_2 (g) → CO_2 (g); $\Delta H = -394.0$ kJ (i)

It is also possible to carry out this reaction in two steps. First, carbon can be converted to CO followed by the oxidation of CO to CO_2 In other words reaction can be considered to be made up of the following two reactions·

C(graphite) + $\frac{1}{2}$ O_2 (g) → CO(g); ΔH_1

$$= -110.5 \text{ kJ} \quad \text{(ii)}$$

CO(g) + $\frac{1}{2}$ O_2 (g) → CO_2 (g); ΔH_2

$$= -283.5 \text{ kJ} \quad \text{(iii)}$$

C(graphite + O_2 (g) → CO_2 (g), $\Delta H_1 + \Delta H_2$
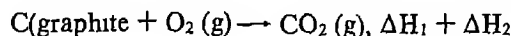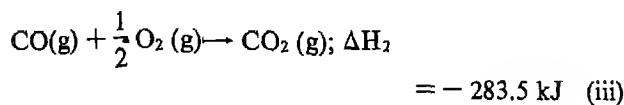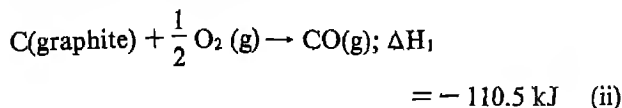
$$= -394.0 \text{ kJ}$$
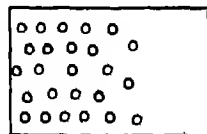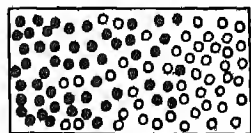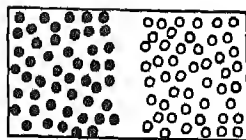
It is clear that ΔH for the reaction (1) is the sum of the enthalpy changes for (ii) and (iii) reactions, i e., $\Delta H = \Delta H_1 + \Delta H_2$.

This additivity leads us to HESS'S LAW OF CONSTANT HEAT SUMMATION The enthalpy change in chemical reaction is the same whether it takes place in one or several stages; if it takes place in several stages the enthalpy of the reaction is the algebraic sum of the enthalpies of reactions of the several stages.

This is a very important law as it provides us a method for determining heats of reaction that cannot be experimentally determined from other heats of reactions which are known. For example, to calculate the C—H bond energy in methane one would like to know the heat of reaction for

$$CH_4(g) \longrightarrow C(g) + 4H(g); \Delta H = ?$$
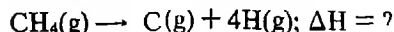
One-fourth of ΔH will give us the C—H bond energy, since the above reaction is limited to the formation of four C — H bonds. To arrive at this we can consider the following reactions:

$$CH_4(g) + 2O_2 \text{ (g)} \longrightarrow CO_2(g) + 2H_2O(l); \Delta H_1 = -891 \text{ kJ}$$
(Heat of combustion of methane)

$$C(s) + O_2(g) \longrightarrow CO_2(g) \; ; \; \Delta H_2 = -394 \text{ kJ}$$
(Heat of combustion of graphite)

$$H_2(g) + \frac{1}{2} O_2 \text{ (g)} \longrightarrow H_2O(l) \; ; \; \Delta H_3 = -286 \text{ kJ}$$
(Heat of combustion of hydrogen)

$$C(s) \longrightarrow C(g) \quad ; \Delta H_4 = +717 \text{ kJ}$$
(Heat of sublimation of graphite)

$$H_2(g) \longrightarrow 2H(g) ; \Delta H_5 = +436 \text{ kJ}$$
(Heat of dissociation of hydrogen molecule)

For

$$CH_4(g) \longrightarrow C(g) + 4H(g)$$
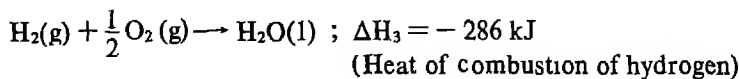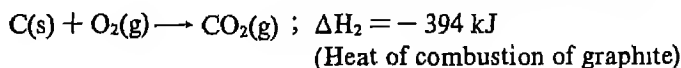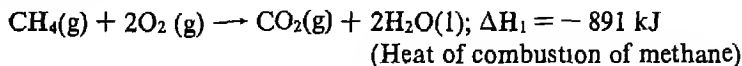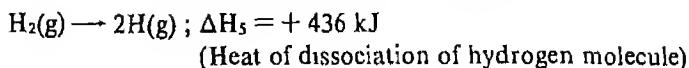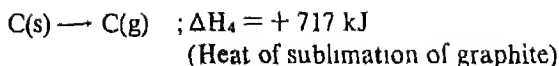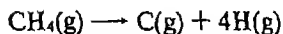
$$\Delta H = \Delta H_1 - \Delta H_2 - (2 \times \Delta H_3) + \Delta H_4 + (2 \times \Delta H_5) = +1664 \text{ kJ}$$

Thus, for $\quad C(g) + 4 H(g) \longrightarrow CH_4(g)$, $\Delta H = -1664 \text{ kJ}$

Therefore the bond energy of $C - H$ bond in methane is $\dfrac{1}{4} \times (1664) = 416 \text{ kJ mol}^{-1}$

8 3 HEATS OF REACTIONS

The amount of heat released or absorbed during a chemical reaction depends on the amount of substance that has reacted.

Let us dissolve 1g of ammonium chloride in 20 cm^3 of water and determine the change in temperature of the water with a thermometer. If we repeat this experiment with different amount of ammonium chloride (say 2 g, 4 g, 5 g, 8 g), keeping the volume of the water constant (20 cm^3), we will find the temperature change to increase with the amount of ammonium chloride dissolved.

The heat of reaction is the amount of heat released or absorbed in a reaction. We now complete our chemical equation by including in it the energy changes that accompany a reaction. For example we would write

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + 572 \text{ kJ at 298 K}$$
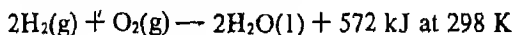
This thermochemical equation, affirms that when 2 moles of hydrogen in the gaseous state combine with 1 mole of oxygen in the gaseous state, 2 moles of water are formed in the liquid state and 572 kJ of energy are released into the surroundings.

For an endothermic reaction the thermochemical equation would be

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) + 63.5 \text{ kJ} \rightarrow BaCl_2.2H_2O(s) + 2NH_3(aq) + 8H_2O(l)$$
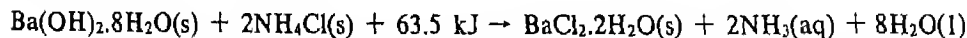
The nature of the energy released depends upon the manner in which the reaction is carried out. If hydrogen-oxygen reaction is carried out by igniting the hydrogen (explosive reaction) the energy would be released in the form of heat, light and mechanical energy. If it is carried out quietly in the presence of a catalyst in what is called a FUEL CELL much of the energy will be released in the form of electricity (such hydrogen-oxygen fuel cells were used in space missions leading to the landing of man on the moon).

8 3 1   Heat of Neutralisation

When a solution of hydrochloric acid is added to a solution of sodium hydroxide dissolved in water, heat is released. The net reaction is the formation of water from the reaction of hydrogen ions with hydroxyl ions

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\ (1) + energy \quad 57.1\ kJ$$
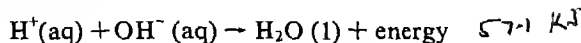
The heat of reaction in this neutralisation of an acid by a base is called the HEAT OF NEUTRALISA-TION Experiments reveal that for all strong acids and bases, the heat of neutralisation is the same when equivalent concentrations of acids and bases are used, e.g., 1M HCl and 1M NaOH; or 0.5M H_2SO_4 and 1M KOH, or 1M HNO_3 and 1M KOH, etc
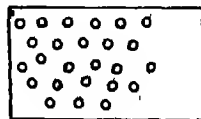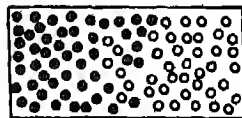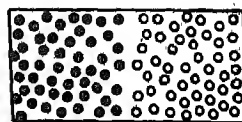
Why is it that heat of neutralisation of strong acids and bases is independent of the acid and base?

It has been determined by careful measurements that when 1 mole of water is formed by the neutralisation of 1 mole of H^+ (aq) and 1 mole of OH^-(aq) ions, 57.1 kJ of energy is released

Example 8.1

What would be the heat released when

(i) 0 25 mole of hydrochloric acid in solution is neutralised by 0 25 mole of sodium hydroxide solution?

(ii) 0.5 mole of nitric acid solution is mixed with 0.2 mole of potassium hydroxide solution?

(iii) 200 cm³ of 0.2 M hydrochloric acid solution is mixed with 300 cm³ of 0.1 M sodium hydroxide solution?

(iv) 400 cm³ of 0.2 M sulphuric acid is mixed with 600 cm³ of 0.1 M sodium hydroxide solution?

(v) Assuming that the specific heat of water is $4.18\ JK^{-1}g^{-1}$ and ignoring the heat absorbed by the container, thermometer, stirrer, etc., what would be the rise in temperature of the solution in the cases of (iii) and (iv)?

Solution

(i) 0.25 mole HCl (aq) + 0.25 mole NaOH (aq)
The net reaction is
H^+ (0 25 mole) + OH^- (0 25 moles) ⎯⎯→ water formed (0.25 mole).
Therefore heat released would be 57.1 × 0.25 kJ = 14.3 kJ
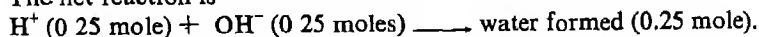
(ii) 0.5 mole HNO_3 (aq) + 0.2 mole NaOH (aq)

The net reaction is

0.2 mole H^+ + 0 2 mole OH^- → 0.2 mole of water formed
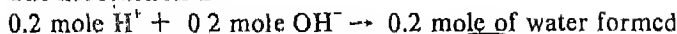
(0 3 mole of H^+ of nitric acid remains unreacted.)

Therefore, heat released would be 57 1 × 0.2 kJ = 11.4 kJ

(iii) 200 cm^3 of 0.2 M HCl solution provides $\dfrac{200 \times 0.2}{1000}$ = 0.04 mole of H^+

300 cm^3 of 0.1 M NaOH solution provides 0.03 mole of OH^-. The net reaction is 0.03 mole of H^+ + 0.03 mole of OH^- = 0.03 mole of water Therefore, heat released would be

$$0 03 \times 57.1 \text{ kJ} = 1 71$$

(iv) 400 cm^3 of 0.2 M sulphuric acid (H_2SO_4) provides $\dfrac{2 \times 0.2 \times 400}{1000}$ mole of

H^+ = 0.16 mole of H^+

600 cm^3 of 0.1 M sodium hydroxide has $\dfrac{600 \times 0 1}{1000}$ = 0.06 mole of OH^-

The net reaction is

0.06 mole of H^+ + 0.06 mole of OH^- = 0.06 mole of water
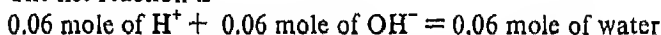
Therefore heat released would be = 0.06 × 57. 1 kJ = 0 31 kJ.

(v) For (iii) mass of solution is approximately 200 g + 300 g = 500 g (Assuming specific gravity of solution = specific gravity of water). Therefore, rise in temperature

$$= \frac{1.71 \times 1000}{500 \times 4.18} = 0.82 \text{ K}$$

For (iv) mass of solution is approximately 400 g + 600 g = 1000 g

Rise in temperature $= \dfrac{0.31 \times 1000}{1000 \times 4 18} = 0 074 \text{ K}$

8.3.2 Heat of Combustion

We noted earlier that society depends on the exothermic combustion reaction of fuels and food with the oxygen in the air for the energy needed for various activities. *Combustion* releases energy as heat and the heat of reaction is called *heat of combustion*. The values are usually quoted for 1 mole of the fuel. The cooking gas in cylinders mainly contains a hydrocarbon (a compound of hydrogen and carbon) called butane, (C_4H_{10}) During the complete combustion of 1 mole of butane (i.e.,

burning butane in excess air), 2658 kJ of heat is evolved We say the heat of combustion of butane to CO_2 and water as gas is 2658 kJ mol^{-1}

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4\,CO_2(g)$$
$$+ 5H_2O(g) + 2658\ kJ$$
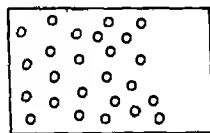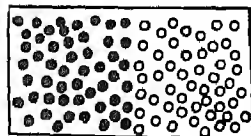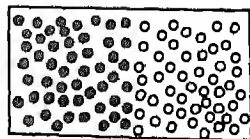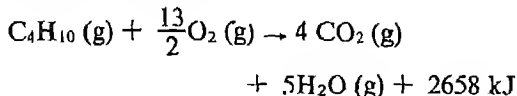
Example 8 2

(i) A cylinder of gas is assumed to contain 11 2 kg of butane. If a normal family needs 20000 kJ of energy per day for cooking, how long will the cylinder last?

(ii) If the air supply to the burner is insufficient (i e , you have a yellow instead of a blue flame) a portion of the gas escapes without combustion. Assuming that 30 per cent of the gas is wasted due to this inefficiency, how long would the cylinder last?

Solution

(i) Molecular formula of butane is C_4H_{10},
Molecular mass of butane is 58 $gmol^{-1}$
58 g of butane on complete oxidation yields 2658 kJ of heat
Therefore 11 2 kg of butane yields ·

$$\therefore \qquad \frac{2658\times11.2\times1000\ kJ}{58}$$

The family needs 20000 kJ per day.
Therefore, the cylinder containing 11.2 kg of butane lasts for

$$\frac{2658\times11\ 2\times1000}{58\times20000}\ \text{days}\ \approx 26\ \text{days}.$$

(ii) Since 30 per cent of the gas is wasted due to inefficiency, the heat yielded per mole of butane will be $= 2658 \times 0.7$ kJ
Therefore the number of days the cylinder will last

$$= \frac{2658\times0.7\times11\ 2\times1000}{58\times20000}\ \text{days}\ \approx 18\ \text{days}$$

The energy required for life is also provided by the metabolism of the food taken by the living organism. If we consider a human being, his or her energy supply is provided mainly by the carbohydrates and fats consumed The carbohydrates are broken down, mainly to glucose or its derivatives as the first step in the body and

we can approximate the glucose requirement as the carbohydrate requirement. The heat of combustion of glucose ($C_6H_{12}O_6$) is given by

$$C_6H_{12}O_6 \text{ (s)} + 6\ O_2 \text{ (g)} \longrightarrow 6CO_2 \text{ (g)} + 6H_2O \text{ (g)} + 2900 \text{ kJ}$$
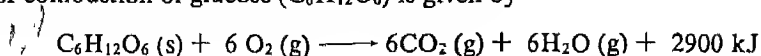
This oxidation reaction, often referred to as the combustion of food, takes place in several small steps and the temperature does not become excessive as we find in the combustion reaction in a flame. Catalysts called enzymes make the reactions possible at body temperature. Further, the energy is released by these oxidation reaction in several steps resulting in the formation of energy-rich molecules, which conserve and deliver the energy at the required site. The chemistry of metabolism (utilisation of food for the several acts of life) is highly intricate and is a marvel

---

HEAT OF FORMATION

The heat of formation is the heat evolved or absorbed when 1 mole of a substance is formed from the standard (most stable) states of its elements. The heat of formation of water and carbon dioxide is written as

$$C \text{ (graphite)} + O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)}; \Delta Hf = -394 \text{ kJmol}^{-1}$$

$$H_2\text{(g)} + \frac{1}{2} O_2\text{(g)} \longrightarrow H_2O \text{ (l)}; \Delta Hf = -286 \text{ kJmol}^{-1}$$
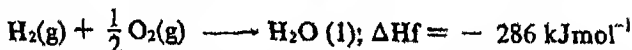
The heat of reaction can be calculated from the heat of formation of reactants and products involved in the reaction, $\Delta H = Hf \text{ (product)} - Hf \text{ (reactant)}$

By convention, the heat of formation of an element in its standard state is zero. Instead of listing the heat of reaction for thousands of reactions most of the data books list standard heats of formation of compounds which are utilised in the calculation of the heat of reactions.

8.3.3   Heat of Fusion and Vaporisation

We need to supply energy to convert 1 mole of ice to 1 mole of water at its melting point, 273 K and 1 atmosphere. This is known as the HEAT OF FUSION of water. When we convert water into steam at 373 K and 1 atmospheric pressure, we again have to provide energy and this is HEAT OF VAPORISATION.

H_2O (s) $+$ 6.01 kJ $\rightarrow$ H_2O(1)
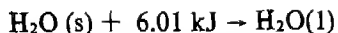
Heat of fusion $=$ 6.01 kJ mol⁻ at 273 K

H_2O (1) $+$ 40.7 kJ $\rightarrow$ H_2O(g)
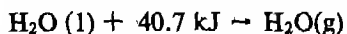
Heat of vaporisation $=$ 40.7 kJ mol⁻ at 373 K
and 1 atm pressure

8.4 SOURCES OF ENERGY

The community requirements of energy mainly are met by the combustion of fuels such as coal, hydrocarbons (kerosene, petrol, natural gas, cooking gas, etc.). These are known as fossil fuels, since they were formed from the remains of extinct life forms when subjected to the high temperatures and pressures in the interior of the earth. Fossil fuels are mainly used in transports (buses, trains, tractors, etc.) and for production of electricity. In addition, charcoal, wood and cow dung are used; recently gobar gas has been introduced as a source of energy in rural areas In all these cases the chemical reaction is the exothermic combustion, and the heat of reaction is converted into other forms of energy. In the production of electricity, for example, the heat is used to convert water into steam, which runs a turbine that generates electricity. The transformation is thus:

```
Chemical                              Mechanical
stored     ------->    Heat   ------->  energy    ------->   Electricity
energy
```
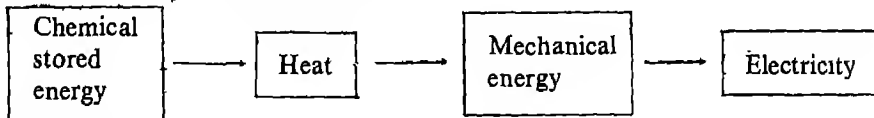
Another important source of energy is the mechanical energy in water, when it is rushing at high velocities (kinetic energy). HYDROELECTRIC POWER stations, such as at Nangal or Shivasamudaram utilise the kinetic energy of fast-moving water to run turbines that generate electricity. In the past few decades man has learned to harness the energy locked in the nucleus of the atom and NUCLEAR POWER stations are being set up in the country. We have nuclear stations at Tarapur (Maharashtra), Kota (Rajasthan) and Kalpakkam (Tamil Nadu). The Narora Station in U.P. is to be commissioned soon. *Wind* is another source of energy which is not yet tapped significantly in India. *Tidal waves, ocean currents*, the hot gases and hot steam that rushes out of the earth's interior in the form of geysers, hot springs, etc. (known as GEOTHERMAL SOURCES are yet other forms of energy awaiting exploitation.

The hydroelectric source and fossil fuels are more readily available and have been exploited immensely. The standard of life and the prosperity of a nation is

reflected to a large extent by the amount of electrical power consumed by its population India is one of those countries which are very backward in this respect (Table 8.1). Coal has been our mainstay and it is only during the last ten years that we have found adequate crude oil (in Assam, Gujarat and from underneath the ocean surface in the Arabian Sea) to be able to meet more than half of our oil demands without imports. Hydroelectricity has also been developed considerably since independence Even then our demands are bound to increase with development and the search for additional sources of energy cannot be allowed to slow down

TABLE 8.1

Consumption of Electrical Energy in India Compared with Consumption in a Few Other Countries

Country	Estimated electrical energy consumption per person per year in (KWH/person/year) (1984-85)
India	220
China	340
Singapore	3500
Great Britain	4700
USSR	5100
Japan	5200
USA	14500

8.4.1 Conservation of Energy Sources and Identification of Alternative Sources

Fossil fuels are sources of energy that nature has formed over the age and at present society consumes them at a rate much faster than their rate of formation It is estimated that man would run out of fossil fuels before the middle of the twenty-

Source	Renewable (Non-depletable) or Non-renewable (Depletable)
Biomass	Renewable
Wind	Renewable
Ocean waves	Renewable
Tidal waves	Renewable
Nuclear fission power	Non-renewable
Solar energy (direct utilisation)	Renewable
Nuclear fusion (this is to create energy the way stars produce energy)	Renewable since hydrogen would be the prime source and is available in plenty.

first century Fossil fuels are termed as 'depletable' or 'non-renewable' sources of energy for this reason

The extent to which river water power can be exploited is also limited and the availability varies between regions. It is imperative that man identify 'alternate sources of energy' Given on page 230 is a partial list of such possible sources

Most of the energy sources (see page 230) are not yet available for exploitation and intense research is on. All of them are more expensive (some of them very much more) than fossil fuels and hydroelectric power. For example, solar energy is so dilute (i.e , diffuse) that a solar power station generating 100 megawatts will occupy $34 \times 10^4 m^2$ (84 acres) compared to 185 m^2 (0.05 acres) occupied by a thermal power station utilising coal Power from nuclear fusion is still very far from practical exploitation. In essence, power is going to be more expensive and hence the need for conservation.
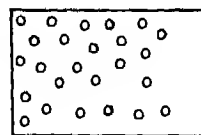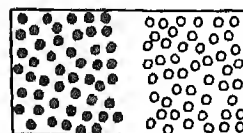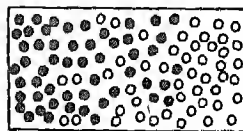
Man has been foolish to fritter away much of the fossil sources of energy It was only in 1974, when the oil prices suddenly shot up, that all the nations woke up to the need for conservation of energy. In fact, one of the main reasons for the drop in oil prices during 1984-87 is that effective conservation has slowed down the growth rate of demand for petroleum products.

In India, we have an additional problem in that a very large fraction of our population (about 75 per cent) depends upon wood for fuel This has led to a large-scale destruction of trees leading to deforestation which leads to change of weather, soil erosion and flooding.

While identification of alternate and renewable sources of energy must be a priority in our effort, we should also practise conservation at all levels. A few practical suggestions for daily life are·

    (a) Use the most efficient of the fuels available to you and preferably an easily renewable one (See Table 8.2).

    (b) When fuel is burnt, efficiency should be high. More efficient stoves (*chullahs*) are being designed. A luminous (yellow) flame indicates insufficient suppy of oxygen and hence incomplete combustion. Compare the heats of reaction under these two circumstances.

$$C(s) + \frac{1}{2} (g) \longrightarrow CO(g); \Delta H = -111 \text{ kJ (incomplete combustion)}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H = -394 \text{ kJ (complete combustion)}$$
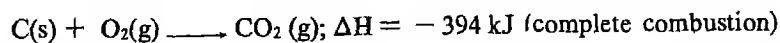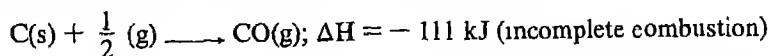
In addition to fuel waste, incomplete combustion leads to the release of poisonous carbon-monoxide.

(c) Your utilisation of the fuel must be planned in such a manner that idle-time is minimised.

(d) Use the correct vessel for cooking. In a vessel larger than required, heat is wasted in heating more of the material of the vessel than necessary. It is better to use a flat-bottomed vessel than one with a round-bottom since more heat escapes from the sides in a round-bottomed vessel. The size of the flame should be adjusted so that heat does not escape from the side of the vessel.

(e) While cooking, use energy-saving devices, such as pressure cookers The cost of your pressure cooker is recovered very quickly since you pay for less fuel.

(f) If you use electricity, turn off lights, fans, pumps, etc., when not needed.

(g) Inspect you electrical connections, such as switches, plug-points, cables, etc , and see that they do not get hot. Heating of electrical connections is very dangerous and can cause fire. It is also an energy wasted.

(h) Think before you cut a tree. Plant two trees if you must cut one.

TABLE 8.2

Comparison of Different Fuels

Fuel	Heating value (kJ/kg)	Cost per unit (1987) (Rupees)	Efficiency of the fuel stove (%)	Annual cost for a family for cooking purposes (20000 kJ/day) (Rupees)
1. Soft coke	27,000	0 80/kg	28	770
2. Charcoal	29,000	3.50/kg	28	3150
3 Wood (sun dried)	16,000	1.20/kg	28	1960

(70 per cent of the energy requirements in villages are met by firewood and other agricultural wastes. Wood-stove efficiencies have been improved and as high as 50 per cent efficiency is now claimed).

Fuel	Heating value (kJ/kg)	Cost per unit (1987) (Rupees)	Efficiency of the fuel stove (%)	Annual cost for a family for cooking purposes (20000 kJ/day) (Rupees)
4. Cow dung	8,800	0.20/kg	11	1510
5 Kerosene	38,000	2.75/kg	48	1100
6. Electricity	3,600 kJ/KWH	0.80/KWH	76	2130
7. Liquid petroleum gas (cooking gas in cylinders)	46,000	4/kg	.60	1060
8. Gobar gas	20,000 kJ/m^3	0.60/m^3	60	360

(The process of production of gobar gas provides in addition a good fertilizer

8.4.2 Pollution Associated with Consumption of Fuels

One of the important causes of pollution of the atmosphere in our cities and towns is the combustion of fossil fuels to meet the needs of society, especially those of electrical power and transport. Carbon dioxide, the main product of combustion is released into the atmosphere and if the percentage of carbon dioxide increases significantly, it is expected that the climate of the region would change—the average temperatures are expected to increase Fossil fuels contain compounds of sulphur and nitrogen, or even sulphur in the elemental form as impurities, and combustion results in the release of oxides of nitrogen and sulphur' which are corrosive and piosonous. They are known to cause 'acid rain' when the rain water turns acidic Besides, the process also releases unutilised hydrocarbons and the poisonous carbon monoxide. Some of the hydrocarbons released are health hazards A large-scale effort is on to minimise the pollution and many countries have achieved significant success. In India, we are still at the pollution-increasing stage.
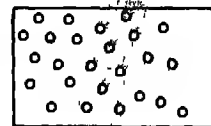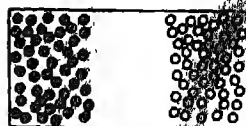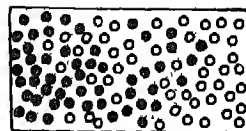
Other sources of energy are also beset with similar or even more difficult problems. In nuclear power stations the release of radioactivity into atmosphere is strictly controlled but disasters occur occasionally (Chernobyl in Russia in 1986 and Three-mile-Island in U.S.A in 1979) and a large segment of population gets affected A more significant problem is the safe storage (for decades) of the radioactive waste (with an extremely high level of radiation) generated by the nuclear power stations.

8.4.3 The Sun as the Primary Energy Source

An examination of the energy cycle given on page 234 reveals that the sun is the ultimate source of energy.

Besides, the formation of elements is now believed to have occurred stepwise from hydrogen by the process of nuclear fusion occurring in stars. In that sense, everything that we see around us, including ourselves and the uranium we use as nuclear fuel, are all children of star dust. Hence, stars in general (and our sun in particular) are the ultimate source of all our energy. It is no wonder that most ancient religions recommend worship of the sun.

8.5 WHAT DECIDES THE DIRECTION OF SPONTANEOUS CHANGE IN A CHEMICAL REACTION?

We have seen that, in nature, we have both exothermic and endothermic reactions
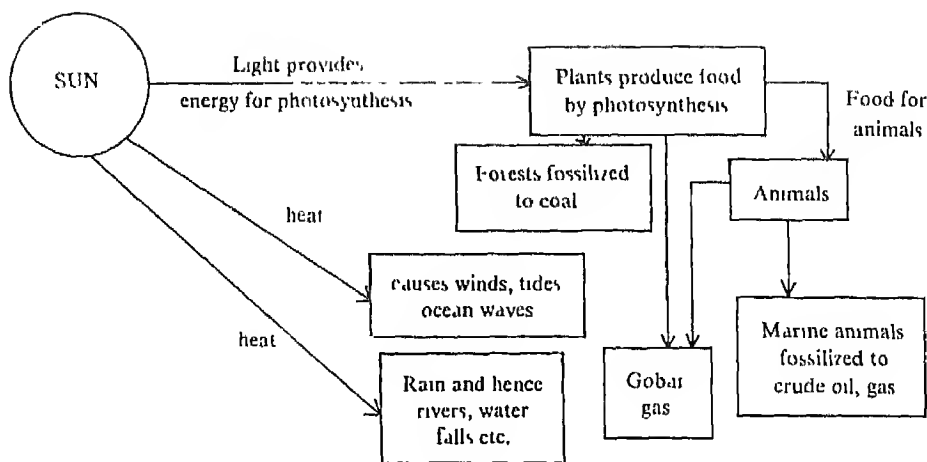
occurring spontaneously* and the products are more stable than the reactants in such cases. A dilemma is immediately apparent—in endothermic reactions, where the enthalpy of products is higher than the enthalpy of reactants and this implies that in this case the products with greater enthalpy are more stable than the reactants.

We are aware that water or any object reaches a state of equilibrium by having minimum gravitational potential energy; water flows down a gradient and objects tend to fall and attain a position such that the centre of mass has the least distance from the centre of the earth. Obviously decrease in enthalpy is not always necessary for a spontaneous chemical reaction.

Let us perform the following experiment:

Take a rubber band; (a) stretch it suddenly and immediately feel its temperature by placing it on the forehead in the stretched condition Is the change exothermic or endothermic? (b) Stretch a rubber band and keep it stretched for some time to allow it to reach room temperature. Then suddenly release it and feel its temperature with the forehead. Is the change exothermic or endothermic?

It is observed that the *natural tendency* of a stretched rubber band is to reach the relaxed state even though it absorbs heat energy from the surroundings (endothermic). This implies that for every change there is a direction of *natural tendency*, irrespective of whether the energy content of the system increases or decreases. The direction of natural tendency is decided by factors in addition to the desired

---

* A reaction that has a natural tendency to occur of its own accord is said to be spontaneous

decrease in energy, we know now that there is only one other additional factor. We shall attempt to understand this factor by performing the following experiments:

Take a tray (about 10 cm square) and divide it into two equal parts. Fill one side with marbles of one colour and other side with clear marbles of the same size and mass. Use enough marbles to leave some space as shown in Fig 8 2. Then shake the tray sideways with a uniform motion and observe what happens to the marbles
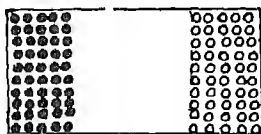
Fig 8 2 *A tray with dark and light marbles separated into two groups*
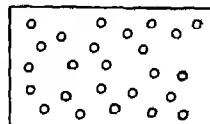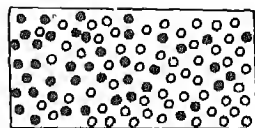
Flip the pages as suggested in Fig. 8 3 (a) and Fig Fig 8 3 (b) and say which is the probable direction. In Fig 8 3(a) you start with marbles of the two colours separated and in Fig. 8.3.(b) you start with the marbles of the two colours completely mixed. Is what is depicted in Fig. 8 3.(b) possible?

The series of pictures in Fig 8 4 represent what happens if we start with a container having all the molecules in one corner (may be done by opening a partition placed on one side) Going backwards (as seen by flipping the figure backwards) that is, starting with all the molecules well spread out and finding that all the molecules have collected on a corner at a later time is 'improbable' A similar observation is made when we watch what happens if we have two different gases (bromine vapour and air) separated into two containers and then the two are connected by opening a tap between them (Fig 8 5)

There is one dominant description that emerges from all the experiments listed above there is a natural tendency for molecules to spread, i e, to go from 'order' to 'disorder'

Fig. 8.3(a)   Fig. 8.3(b)   Fig. 8.4
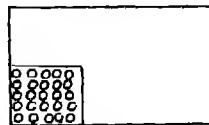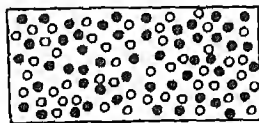
Fig 8 3 (a) *We start with a tray of the marbles as in Fig 8 2 Flip the pages backwards (from page215 containing Fig 8 3(a) What do y . . . . i. i. . . .'.*
Fig. 8.3 (b) *We start with a tray of the . . . . mixed up. Flip the pages backwards (from page 215 containing Fig . . . . Is this possible?*
Fig. 8.4 *You start with a container which has a partition and gas is fed into the enclosed space The partition is removed, see what happens. Flip both ways and decide which is the spontaneous direction?*
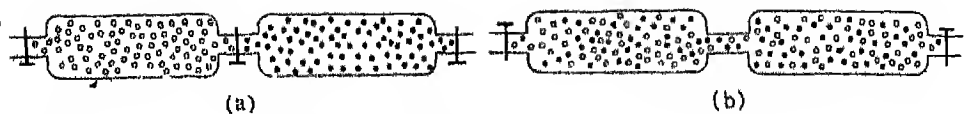
Fig. 8 5 *Mixing of bromine vapour and air* **(a)** *situation before mixing,* **(b)** *situation after a few hours*

Hence all natural processes tend to follow two criteria, decrease energy content and go from order to disorder Just as we measure energy in joules, can we measure the extent of order or disorder in any unit? A tremendous advance was made in our understanding of natural processes, when the concept of 'entropy' was introduced At this juncture, it is sufficient to define 'entropy' as a quantity that measures order and disorder in a system and increases when order decreases and disorder increases The natural tendency in nature is the tendency to increase entropy. For example, in all the experiments described above the tendency to decrease order and increase entropy is the natural tendency. Entropy is measured in units of joules per degree kelvin (JK^{-1}).

Let us consider chemical reactions which are of our immediate concern. We have seen that reactions tend to seek minimum energy and maximum randomness, i.e., a reaction will be more probable if it is exothermic or there is an increase in entropy Now if entropy is denoted by S and entropy change by ΔS, chemical changes will have natural tendency to occur if ΔH is negative and ΔS is positive But contrary to this, we also come across reactions which are endothermic in nature, i.e., ΔH is positive and still they occur. Similarly there are also reactions in which entropy of the system decreases but occurs. Scientists found that while deciding the natural tendency for a reaction to occur (spontaneity) one should consider both ΔH and ΔS together. The function that takes both enthalpy and entropy into account is called, FREE ENERGY and is given the symbol G (meaning Gibb's free energy after the name, J. Willard Gibbs). The relation between G, H and S is

$$G = H - TS$$

and the change in free energy, ΔG at constant temperature and pressure can be written as

$$\Delta G = \Delta H - T \Delta S$$

(Here, T is temperature in Kelvin)

Thus, the criterion for a reaction to occur spontaneously will be decided by ΔG. It has been found that irrespective of the signs of ΔH and ΔS, a reaction will be spontaneous if ΔG value is negative i.e., free energy of the system decreases. For a spontaneous reaction,

$$G_{products} - G_{reactants} = \Delta G < 0.$$

A reaction for which ΔG value is zero will be at equilibrium, i.e ,

$$\Delta G_{equilibrium} = 0$$

But if ΔG is positive, i e., $\Delta G \geq 0$, the reaction is non-spontaneous The reverse of the reaction, however, will be spontaneous.

The most favourable circumstance for a negative value of ΔG, which indicates a spontaneous reaction, is a negative value of ΔH together with a positive value of ΔS However, a large negative value of ΔH may outweigh even an unfavourable entropy change and ΔG value may be negative resulting in spontaneity of a reaction.

Similarly, a large value of entropy change, ΔS together with suitable temperature values ($T\Delta S$) may also outweigh an unfavourable enthalpy change, giving rise to a negative value of ΔG

The following Table summarises how signs of ΔH and ΔS for a given reaction determine the reaction spontaneity.

TABLE 8 3

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Remarks
−	+	−	Reaction spontaneous at all temperatures
+	−	+	Reaction non-spontaneous at all temperatures
−	−	− (at low T) + (at high T)	Reaction spontaneous at low temperatures Reaction non-spontaneous at high temperatures
+	+	+ (at low T) − (at high T)	Reaction non-spontaneous at low temperatures Reaction spontaneous at high temperatures

If we see the above Table we find that temperature plays a very important role in deciding the spontaneity of a reaction. A reaction/process may not be spontaneous

at a low temperature but may be spontaneous at a slightly higher temperature or vice versa. This is illustrated in the conversion of ice into water.

Ice ⟶ Water
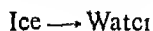
Temperature (T)		ΔH	ΔS	TΔS	ΔG
(°C)	(K)	(Joules)	(Joules K⁻¹)	(Joules)	(Joules)
−10	263	5614	20 5	5392	+ 227
0	273	6006	22 0	6006	0
+10	283	6391	23.4	6622	− 231

It is seen that at all temperatures, ΔH is positive, i.e., we have to supply heat to melt ice into water ΔS is also positive since solid ice has a more ordered structure than liquid water. However the sign of ΔG changes with temperature:

(i) At 263K, ΔG>0, indicating that ice is more stable than water; (ii) at 283K, ΔG<0 indicating that ice is less stable than water; and (iii) At, 273K, ΔG = 0 indicating equilibrium between ice and water.

We thus conclude that it is the interplay of entropy and enthalpy changes that decides the direction of spontaneous change.

8.6   WHY THE ENERGY CRISIS IF ENERGY IS CONSERVED IN NATURE ?

In the section 8 5, we have seen several processes that appeared predestined to go only one way, i.e, the direction in which disorder increases. Starting from the situation in Fig 8.5 (a) where the bromine molecules are separated from the molecules of the air, the most probable distribution after a long time is what is depicted in Fig 8.5(b). The probability of other distributions (say one in which 75 per cent of the bromine molecules are in the right-hand container) is very much less than in Fig. 8 5 (b). The probability that the distribution may return by chance to what (as shown in Fig. 8.5(a) is extremely small and may be considered near zero To return from Fig 8.5(b) to 8.5(a) one would have to perform a series of actions, such as physically separating bromine molecules from the rest and then filling the two containers, and all this involves work and hence expenditure of energy.

In a similar way, burning of fuels is a 'one-way process' and to reform the fuel, say coal from the carbon dioxide released into the air, considerable effort is needed by nature (through the act of photosynthesis). It is this 'one-way' property of most processes that we shall, in later years, see, is responsible for all engines to be less than hundred per cent efficient, i e.

$$\frac{\text{Work done by the engine}}{\text{Energy fed into the engine}} \text{ is always less than 1}$$

Even though energy is conserved, a portion of it is always converted into those forms which cannot be recycled without great effort (i e., the amount that goes into increasing entropy) Therefore, the concept of useful work leads to

$$\Delta G = \Delta H - T\Delta S = \text{maximum useful work}$$

ΔG really decides for us how much work we can, at best, derive from any process

A precise way of stating the energy crisis is " the world's energy remains constant but it is being converted by the act of living into forms which are more expensive and less convenient to use "

EXERCISES

8 1   Fill in the blanks
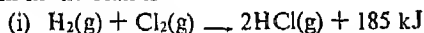
(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 185 \text{ kJ}$
This reaction is —— thermic (exo or endo?)
$\Delta H = $ —— kJ

(ii) $H_2(g) + 1/2 \, O_2(g) \longrightarrow H_2O(l)$
$\Delta H = -286 \text{ kJ}$
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ —— kJ ($\pm$?)
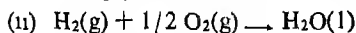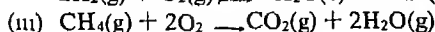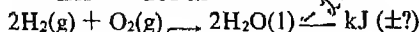
(iii) $CH_4(g) + 2O_2 \longrightarrow CO_2(g) + 2H_2O(g)$
$\Delta H = -809 \text{ kJ}$

The calorific or fuel value of 1 kg of $CH_4(g)$ is —— kJ/kg

8.2   (i) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O, \; \Delta H = -2878 \text{ kJ}$
ΔH is the heat of —— of butane gas
(combustion)
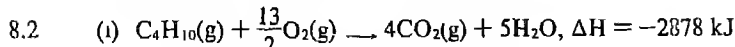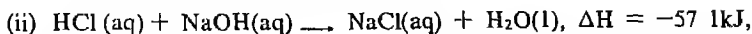
(ii) $HCl \text{ (aq)} + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l), \; \Delta H = -57 \, 1\text{kJ},$
in real terms, $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$
ΔH is the heat of —— of hydrochloric acid and sodium hydroxide solutions.
(neutralisation)

(iii) $C(s) \longrightarrow C(g) \; , \quad \Delta H = 716.7 \text{ kJ}$
(graphite)
ΔH is the heat of —— of graphite
(sublimation)

(iv) $C(s) \longrightarrow C(g);\ \Delta H = 714.8\ kJ$
        (diamond)
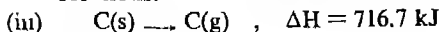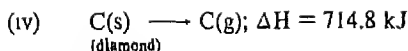
ΔH is the heat of —— of diamond.

(v) $H_2O(s) \longrightarrow H_2O(l)\ ;\ \Delta H = 6.01\ kJ$
     ΔH is the heat of —— of ice

(vi) $H_2O(l) \longrightarrow H_2O(s) \cdot \Delta H = -6.01\ kJ$
      ΔH is the heat of —— of water.

(vii) $H_2O(l) \longrightarrow H_2O(g)\ ;\ \Delta H = 40\ 7$
       ΔH is the heat of —— of water.
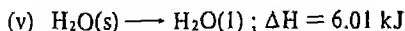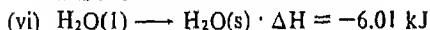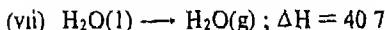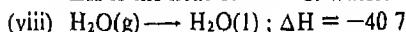
(viii) $H_2O(g) \longrightarrow H_2O(l)\ ;\ \Delta H = -40\ 7$
        ΔH is the heat of —— of steam.

8.3   Calculate the heat of combustion of glucose from the following data:
      $C(graphite) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -395.0\ kJ$
      $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l)\ ,\ \Delta H = -269\ 4\ kJ$
      $6C\ (graphite) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)$
                                                (glucose)
                                $\Delta H = -1169.8\ kJ$
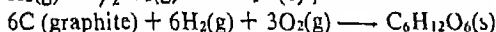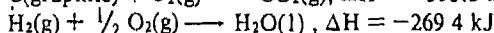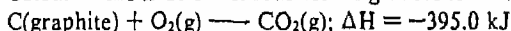
8 4   Calculate the entropy change ΔS per mole for the following reactions.
      (i)   combustion of hydrogen in a fuel cell at 298 K
            $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(g)$
                $\Delta H = -241.60\ kJ$
                $\Delta G = -228.40\ kJ$
      (ii) Vaporisation of methanol at its normal boiling point.
            Methanol (l) $\longrightarrow$ methanol(g) ; $\Delta H_{vap} = 23.9\ kJ$
                        Boiling point = 338 K
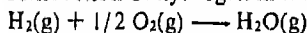
8 5   Calculate the free energy change per mole for the following reactions.
      (i) $CaCO_3(a) \longrightarrow CaO(s) + CO_2(g)$ at 298 K
                        $\Delta H = 177.9\ kJ$
                        $\Delta S = 160.4\ JK^{-1}$
      (ii) $2NO_2(g) \longrightarrow N_2O_4(g)$ at 298 K
                        $\Delta H = -57\ 2\ kJ$
                        $\Delta S = -175\ 6\ JK^{-1}$

8 6   Calculate the $C — C$ bond energy from the following data:
      $2C(graphite) + 3H_2(g) \longrightarrow C_2H_6(g)\ ,\ \Delta H = -84.67\ kJ$
      $C(graphite) \longrightarrow C(g);\ \Delta H = 716\ 7\ kJ$
      $H_2(g) \longrightarrow 2H(g);\ \Delta H = 435\ 9\ kJ$
      Assume 416 kJ as the C--H bond energy.
      Express it in kJ mol^{-1}.
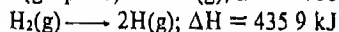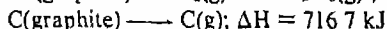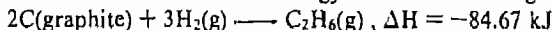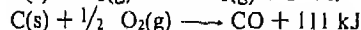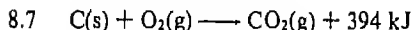
8.7 $C(s) + O_2(g) \longrightarrow CO_2(g) + 394\ kJ$
      $C(s) + \frac{1}{2}\ O_2(g) \longrightarrow CO + 111\ kJ$
      (i) In an oven using coal (assume the coal is 80 per cent carbon in weight), insufficient
           oxygen is supplied such that 60 per cent of carbon is converted to CO_2 and 40 per

cent of carbon is converted to CO_2 and 40 per cent carbon is converted to CO. Find out the heat generated when 10 kg of coal is burnt in this fashion

(ii) Calculate the heat generated if a more sufficient oven is used so that only CO_2 is formed

(iii) Calculate the percentage loss in heating value for the inefficient oven

8 8   Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane The heat of combustion of methane to CO_2 and water as gas is given by.

$$CH_4(g) + 2O_2 (g) \rightarrow CO_2(g) + 2H_2O(g) + 809 \text{ kJ}$$
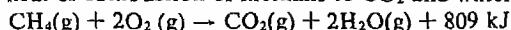
How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20000 kJ of energy per day to meet all its needs and that the methane content in gobar gas is 80 per cent by weight?

8 9   (i) An average person needs about 10000 kJ per day How much carbohydrates (in mass) will he have to consume, assuming that all his energy needs are met only by carbohydrates, in the form of glucose?

(ii) A human eats 0 350 kg carbohydrates (glucose) and 200 g of fats every day, and it is assumed that combustion of fats can produce energy equivalent to 39000 kJ kg^{-1} If the body consumes all the carbohydrates preferentially, how much will his weight increase per year, assuming that only 50 per cent of the excess fats are excreted

8 10 If a man submits to a diet of 9500 kJ per day and expends energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg? (Ignore water loss for this problem)

8.11 Fill in the blanks in the following table related to $H_2O(1) \longrightarrow H_2O$ (steam)   at standard atmospheric pressure

$t°C$	T K	ΔH (Enthalpy change) $kJ \text{ mol}^{-1}$	ΔS (Entropy change) $J \text{ mol}^- K^{-1}$	$T\Delta S$ kJ	ΔG (Free Energy) kJ
90	363 0	41 1	—	—	+ 1.193
100	373 0	40. 7	109	—	—
110	383 0	40.1	—	—	−0 979

8 12 In the following changes state whether order has increased or decreased and consequently the direction of change of entropy of the system.

(i) Stretched rubber band $\longrightarrow$ Loose rubber band

(ii) $H_2O(1) \longrightarrow H_2O(s)$

(iii) Dry ice (solid carbon-di-oxide) $\longrightarrow CO_2(g)$

(iv) Steam $\longrightarrow$ Water

(v) $Cr^{3+} + 6H_2O(aq) \longrightarrow Cr(H_2O)_6^{2+}$

(vi) $CO_2 + H_2O \xrightarrow[\text{Photosynthesis}]{\text{light}}$ carbohydrates $+ O_2$

(vii) Proteins (helical form) $\underrightarrow{\text{denaturation}}$ proteins (random coil form)

(viii) Normal egg $\longrightarrow$ hard boiled egg

8 13   Consider the reaction

A + B → C + D

(i) If the reaction is endothermic and spontaneous in the direction indicated, comment on the sign of ΔG and ΔS

(ii) If the reaction is exothermic and spontaneous in the direction indicated, can you comment on the sign of ΔG and ΔS?

(iii) If the reaction is exothermic and spontaneous only in the direction *opposite* to that indicated, comment on the sign of ΔG and ΔS for the direction indicated in the equation

UNIT 9

CHEMICAL EQUILIBRIUM

What can we do when we cannot
go backward or forward ?

OBJECTIVES

In this Unit, we shall learn

* the dynamic nature of equilibrium in physical and chemical processes;

* the derivation of mathematical expression for the equilibrium constant and its aplication in finding out the extent of a chemical change;

* the characterstics of the equilibrium state in terms of constancy of macroscopic properties;

* the effect of concentration, pressure and temperature on the equilibrium state,

* the concept of acids-bases and pH;

* the application of the law of equilibrium to ionic systems such as ionisation of electrolytes (including acids-bases); and solubility of sparingly soluble salts.

FROM OUR EXPERIENCE in carrying out chemical reactions, we are led to believe that, when we mix reactants in the exact proportion required, and perform a chemical reaction, all the reactants are converted into products with the release or absorption of energy This assumption is a central one in chemical analysis, especially when you determine quantitatively the amount of a particular substance contained in a system by volumetric or gravimetric analysis using stoichiometry (chemical arithmetic). This is *not* true in all cases. Many chemical reactions proceed only to a certain extent and the resulting mixture contains both reactants and products. We then say that a CHEMICAL EQUILIBRIUM is reached and the properties of the mixture remain constant with time. In this Unit we will examine many aspects of chemical equilibrium. By changing conditions of the system, such as temperature, pressure, concentration of reactants, and by changing concentration of products by the act of removing them from the site of the reaction, etc., we can control the extent to which a reaction can proceed. This is an important aspect that plays a crucial role in the design of industrial processes.

Let us add 10 cm^3 of 0.1 M lead nitrate solution to 10 cm^3 of 0.1 M potassium chromate solution The solution is filtered and to the filtrate, a few drops of potassium chromate is added. Let us examine if more precipitate is formed At first the yellow precipitate of lead chromate is formed and the reaction goes to (very) near completion. If the exactly required amounts of reactants had been mixed as per the following equation,

$$Pb(NO_3)(aq) + K_2CrO_4(aq) \rightarrow PbCrO_4(s) + 2KNO_3(aq)$$
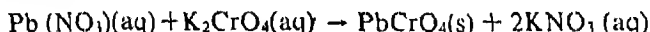
the filtrate would not have formed any precipitate, when potassium chromate solution was added again. This is an example of a reaction which goes almost to completion. (Why we say 'almost to completion' instead of 'to completion' will be understood later on when we consider what is known as the 'solubility product' in this Unit

When a bottle of ammonia solution *(Be Careful. Use Only a Very Dilute Solution—less than 0 1 M)* is opened you immediately smell the ammonia In water the reaction is.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
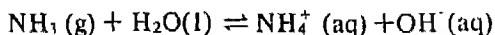
Ammonium ion (NH$_4^+$) does not have any smell. Therefore from the smell we infer that all the NH$_3$(g) has not been converted into NH$_4^+$ (aq). The solution is basic (litmus test) due to the presence of OH$^-$ ions

In cases such as in the above experiment, we say that the substances in the final reaction mixture are in state of *chemical equilibrium*. We use the symbol $\rightleftharpoons$ to denote equilibrium as in the above equation in contrast to the symbol $\rightarrow$ used in the earlier equation where the reaction goes to completion. In the latter case when

the substances in the right hand side of the equation are mixed, significant amounts of substances in the left hand side are formed. Therefore, there is no clear distinction between products and reactants and we call all the species present in the equilibrium reaction as reactants

When the ammonia solution in the previous experiment is boiled no smell of ammonia will emerge from the solution after some time. The solution when tested for OH⁻ (litmus test) and for NH_4^+ (There is a reagent called Nessler's reagent which can give a test for NH_4^+ in solution) indicates their absence Similarly ammonia can be removed from the solution by bubbling air through the solution We shall understand this later.

9.1   EQUILIBRIA INVOLVING PHYSICAL CHANGES

The characteristics of systems at equilibrium are more easily understood if we examine some physical changes in a state of equilibrium. The most familiar examples involve changes of state such as

$$\text{solid} \rightleftharpoons \text{liquid}$$
$$\text{liquid} \rightleftharpoons \text{gas}$$
$$\text{solid} \rightleftharpoons \text{gas}$$
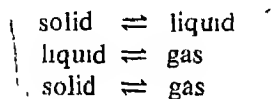
and we shall consider some of them

9.1.1   Solid-Liquid Equilibrium

When placed inside a perfectly insulated thermos flask, such that there is no exchange of heat between its contents and the surroundings, ice and water at 273 K and at normal atmospheric presssure reveal to us many of the important characteristics of an equilibrium state. Firstly, we should notice that the mass of ice and water will not change. The temperature will not change If we could observe the individual molecules of ice and water we would notice that there is considerable activity, in the sense that some molecules from the liquid water join on to the ice and that some molecules of ice pass on to the liquid Since there is no change of mass of ice and water, the rate of transfer of molecules from ice into water and the rate of reverse transfer from water into ice must be equal In terms of free energy change, that you studied in Unit 8, we say that for ice and water system,

$$\Delta'G = 0 \text{ at } 273 \text{ K and standard atmospheric pressure}$$

We also saw that at other temperatures for

$$\text{ice} \rightleftharpoons \text{water}$$

$$\text{or } H_2O \text{ (s)} \rightleftharpoons H_2O \text{ (l)}$$
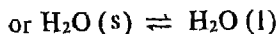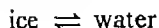
$$\Delta G < 0 \text{ at temperatures greater than 273 K}$$

$$\text{and } \Delta G > 0 \text{ at temperatures less than 273 K.}$$

From this you should infer that ice and water are at equilibrium only at a particular temperature *For any pure substance at 1.00 atmospheric pressure the temperature at which the solid and liquid phase are at equilibrium is called the normal melting point or normal freezing point of the substance.* The equilibrium in this case will be DYNAMIC EQUILIBRIUM

Thus from the above, we infer that in any system at dynamic equilibrium,

    i) Free energy change, $\Delta G = 0$.

    ii) Two opposite changes occur at the same time.

    iii) These two changes occur at the same rate so that the mass on both sides of the equilibrium undergoes no change.

9.1.2 Liquid-Gas Equilibrium

It is common experience that even though the temperature of Delhi (or Jaipur or Hyderabad) and the temperature of Bombay (or Madras or Calcutta) be the same on a particular day, you sweat more at Bombay (or Madras or Calcutta), especially during the summer months. We usually say that the humidity is high in cities which are close to a sea or any large body of water. How can we explain this? The following simple experiment would help us to understand the reasons.

A box carrying a U-tube with mercury (manometer), is made dry by placing some drying agent like anhydrous calcium chloride (or phosphorus pentoxide) for a few hours and then removing the drying agent (Fig. 9 1). By tilting the box on one side, a watch glass (or petri dish) containing water is quickly pushed inside the box. We then watch the manometer It will be observed that the fluid level in the right limb of the manometer will slowly increase and finally reach a constant value, that is, the pressure inside the box has increased and reached a constant value You may also notice, that the volume of water in the watch glass has decreased. Repeat the experiment with different amounts of water in the watch glass, ensuring that you start with a dried box every time.

Initially, there is no water vapour (or very little) inside the box and as the water evaporates the pressure in the box increases due to the addition of water molecules into the gaseous phase inside the box. Since the temperature is held constant, the rate of evaporation will be constant However, the rate of increase in pressure decreases with time leading to a final situation (or equilibrium condition) where there is no *net* evaporation. This implies that as the number of water molecules in the geascous state increases, the rate of the return of the water molecules from the gaseous state into the liquid state increases and when equilibrium is reached,

<center>rate of evaporation = rate of condensation</center>

and the dynamic equilibrium can be written as.

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$
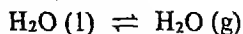
When the equilibrium is reached, the pressure exerted by the water molecules

remains constant and this is called the EQUILIBRIUM VAPOUR PRESSURE of water (or just vapour pressure of water) and it will vary with temperature. When the temperature increases the vapour pressure increases. It is also noticed that so long as there is adequate water in the watch glass, the final equilibrium vapour pressure is independent of the amount of water in the watch glass.
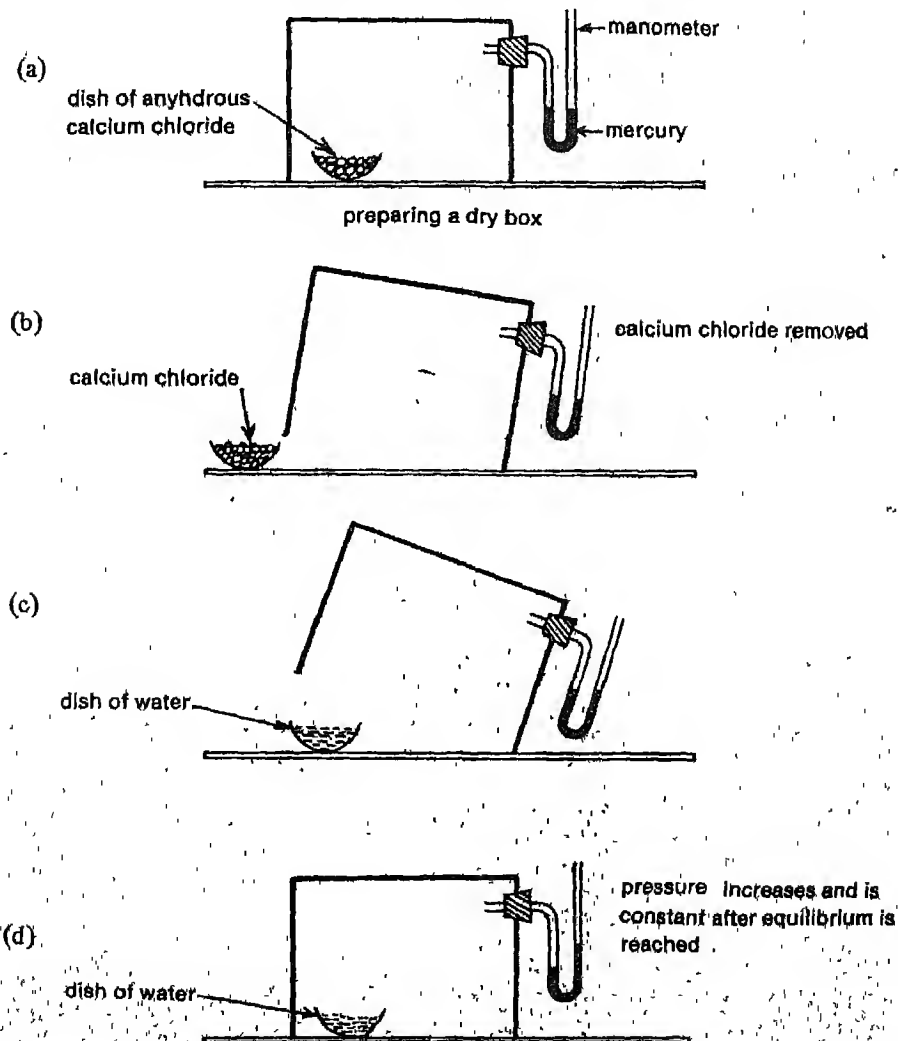
Fig. 9.1 · A scheme for measuring vapour pressure of water

If the same experiment is repeated in a room where the temperature is higher (in summer a closed room gets warmer than a well-ventilated open room) the equilibrium pressure would be observed to be higher If the experiment is repeated with methyl alcohol, ethyl alcohol and acetone, it would be noticed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour press   ·   · ···   Does the intensity of the smell given by a liquid depend on the   ·   ? Are perfumes volatile?

Let us expose three watch glasses containing 1 cm³ each of acetone, ethyl alcohol and water to air without box We then repeat the experiment with 2 cm³ of each of ethyl alcohol and water in a warmer room.

It is observed that in these cases the liquid eventually disappears and the time taken for complete evaporation depends on the nature of the liquid, the amount of the liquid and the temperature

When the watch glass is open to the atmosphere, the rate of evaporation is still constant but since the molecules get dispersed into a large (open) volume the rate of condensation from gas to liquid state can never equal the rate of evaporation. Such systems are said to be *open* and the systems such as a closed box (as mentioned above) are *closed systems* One cannot reach equilibrium in an open system

We thus infer.

In a closed system there is a dynamic equilibrium between molecules in the gaseous state and the liquid state (if sufficient amount of liquid is present). For example,

$$H_2O\,(l) \;\rightleftharpoons\; H_2O\,(g)$$
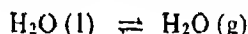
The vapour pressure exerted by the molecules in the gaseous phase is constant at equilibrium. The equilibrium vapour pressure depends upon the liquid (its volatility), temperature and not on the amount of liquid present after equilibrium is reached. It is also independent of the volume of the container for the gaseous state. ,

Our atmosphere is an open system and the water vapour in the air would depend on the amount of water in the area, the wind velocity, temperature, etc Near a sea or a lake, especially when the wind is not high the amount of water vapour in the air at a given temperature is high (as in Calcutta, Bombay or Madras) compared to a city in Rajasthan (almost a desert), Delhi or Hyderabad.

Example 9.1

Liquid	Equilibrium vapour pressure at 293 K (kPa)
water	2 34
acetone	12.36
ethanol	5 85

Which of these will have the lowest and highest boiling points? At 293 K which of these will evaporate least in a sealed container before equilibrium is established?

(Remember 1 atmosphere =101.3 kPa)

Solution

We know that when temperature rises, vapour pressure of the liquids also rises and at boiling point, vapour pressure becomes equal to atmospheric pressure A liquid with lower vapour pressure will require higher temperature for getting its vapour pressure raised equal to atmospheric pressure Therefore, the liquid with the lowest vapour pressure will have the highest boiling point and the liquid with the highest vapour pressure will have the lowest boiling point Out of the three liquids (water, acetone, and ethanol) acetone will have the lowest boiling point and water will have the highest boiling point

At 293 K water will evaporate least in the sealed container before equilibrium is established

9 1.3 Equilibrium Involving Dissolution of Solids in Liquids or Gases in Liquids

Solids in Liquids: It is common knowledge that you cannot dissolve any amount of salt or sugar in a given amount of water If you make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals will separate if you cool the syrup We call a solution in which more solute cannot dissolve, a saturated solution The concentration of the solute in a saturated solution depends upon the temperature In a saturated solution, a dynamic equilibrium exists between the molecules in the solid state and the molecules in the solution

Sugar (in solution) $\rightleftharpoons$ Sugar (solid)
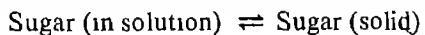
and at equilibrium,

Rate of dissolution of sugar $=$ Rate of precipitation of sugar

Equality of the two rates and dynamic nature of equilibrium can be demonstrated with the help of radioactive sugar (Fig. 9.2) If we drop radioactive sugar into a saturated solution of non-radioactive sugar, it will be observed that the solution and the rest of the sugar existing as solid will also become radioactive
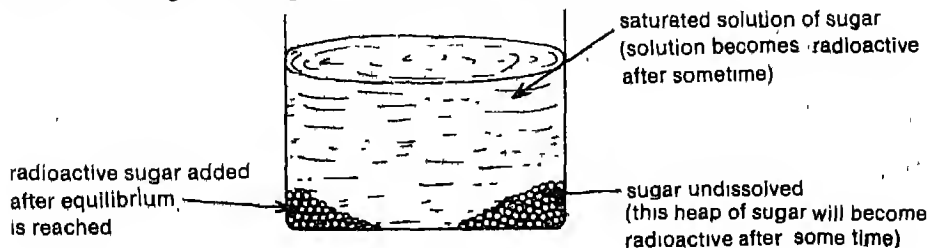
Fig. 9.2 *Demonstration for dynamic nature of chemical equilibrium*

Gases in Liquids   We are aware that when a soda water bottle is opened, the carbon dioxide gas dissolved in it fizzes out rapidly. Here again is an equilibrium situation At a given pressure, there is an equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid. For example,

$$CO_2(gas) \rightleftharpoons CO_2 \text{ (in solution)}$$

William Henry states this in a law called HENRY'S LAW. The mass of a gas dissolved in a given *mass* of a solvent at any temperature is proportional to the pressure of the *gas* above the solvent. This amount decreases with increase of temperature Since the soda bottle is sealed when the gas is at high pressure (above atmospheric pressure), there is plenty of gas dissolved in the water and the gas pressure above the liquid is high As soon as the bottle is opened, the dissolved gas escapes to reach a new equilibrium condition required for the lower pressure, namely atmospheric pressure. If you leave the soda bottle open to the air for some time, it does not fizz anymore, it has turned 'flat'

Example 9.2
If 0.200 g of iodine is stirred in 100 cm³ of water at 288 K till equilibrium is reached what will be the mass of iodine found in solution and the mass that is left undissolved. After equilibrium is reached with 0 200 g of iodine and 100 cm³ of water, we add 150 cm³ of water to the system How much iodine will be dissolved and how much will be left undissolved and what will be the concentration of iodine in solution?

$$[I_2 (aq)]_{\text{at equilibrium}} = 0.0011 \text{ mol} / \text{lit} - 1$$

Solution
Molecular mass of iodine, $I_2 = 254$
At equilibrium the amount of iodine dissolved in 1 litre (1000 cm³) of water

$$0.0011 \times 254$$

$$= 0.2794 \text{ g}$$

$$= 0.28 \text{g}$$

Therefore, mass of dissolved iodine in 100 cm³ = 0.028g
Mass of undissolved iodine in 100 cm³ = (0.200 − 0.028)g .

$$= 0.172 \text{ g}$$

After equilibrium between 0 200 g of I₂ and 100 cm³ of water is reached, addition of 150 cm³ of water will result in further dissolution of I₂

Now dissolved iodine in 250 cm³ of water $= \dfrac{0.28 \times 250}{1000} = 0.070$ g of iodine.

Undissolved iodine = 0.200 g − 0.07 g = 0.130 g

9 1 4 General Characteristics of Equilibria Involving Physical Processes

We noted that

(i) in the case of liquid $\rightleftharpoons$ gas equilibrium, the pressure of the gas above liquid was constant at equilibrium at a given temperature.

(ii) for solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature (melting point) at which the two phases can coexist and without any exchange of heat with the surroundings the mass of the two phases remain constant.

(iii) for dissolution of solids in liquids the solubility is constant at a given temperature.

(iv) for dissolution of gases in liquids the concentration of a gas in liquid is proportional to the pressure of the gas over the liquid, i.e., the concentration of the gas in the space above the liquid.

These four concentration-related findings are expressed in the table below.

Process	Expression that states the findings above: the expression has a constant value for a given condition
$H_2O(l) \rightleftharpoons H_2O(g)$	p_{H_2O} at constant temperature
$H_2O(l) \rightleftharpoons H_2O(s)$	Melting point at constant pressure
Sugar (s) $\rightleftharpoons$ Sugar (solution)	[Sugar (solution)] at constant temperature
$CO_2(g) \rightleftharpoons CO_2(aq)$	$\dfrac{[CO_2(aq)]}{[CO_2(g)]}$ at constant temperature

From the physical changes discussed by us we can state that *the characteristics common to the systems at equilibrium are as follows:*

1. *The system has to be closed; that is it should not gain matter from the surroundings nor lose matter to the surroundings.*
2. *There is a dynamic but stable condition* Two opposite processes occur at the same rate.
3. *The measurable properties of the system remain constant,* since the concentration of the substances remain constant.
4. *When equilibrium is attained, there exists an expression involving concentration of reacting substances which reaches a constant value at a given temperature.* The table above lists the concentration-related expressions for certain physical processes.
5 *The magnitude of the constant value of the concentration-related expression is an indication of the extent to which the reaction proceeds before reaching equilibrium.*

9.2 EQUILIBRIA INVOLVING CHEMICAL SYSTEMS

We have seen that not all chemical reactions proceed to completion; just as in physical processes we reach a state of equilibrium. In fact, no reaction truly goes to completion. We shall soon see that what we mean by completion is that in the final

state of equilibrium, the concentration of reactants (those on the left hand side of an equation) is negligibly small compared to the concentration of the products (those on the right hand side of an eqution); for example,

$$AgNO_3 (aq) + NaCl(aq) \quad \rightleftharpoons \quad NaNO_3(aq) + AgCl(s)$$
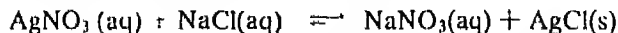
We may add a small arrow in the reverse direction to indicate that at equilibrium the reaction proceeds far to the right. In this Unit, we shall not make such distinctions and assume that arrows $\rightleftharpoons$ indicate equilibria and do not say anything about the relative concentrations of the species involved.

In order to understand equilibrium in a chemical system, let us take the following reaction and perform the experiment:

$$Fe^{3+}(aq) + SCN (aq) \quad \rightleftharpoons \quad FeSCN^{2+}(aq)$$
(yellow)   (colourless)   (deep red)
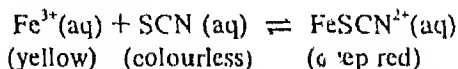
Let us first prepare the following solutions and observe their colour.

a) 200 cm³ of 0.002 mol L⁻¹ potassium thiocyanate soluton, and

b) 200 cm³ of 0.20 mol L⁻¹ iron (III) nitrate solution

Here, we find that solution (a) is colourless and that (b) has a pale yellow colour. In both these solutions the species exist as ions; K^+ and SCN^- in (a) and Fe^{3+}, NO^- in (b).

c) Let us add one drop of solution (a) to 10 cm³ of (b). The solu .on turns reddish brown and this colour is due to the species $FeSCN^{2+}$ in solu .n, which is deep red. The concentration of $FeSCN^{2+}$ can be estimated by the intensity of the colour

d) In a 100 cm³ beaker, let us prepare 50 cm³ of 0.001 mol L⁻¹ solution of potassium thiocyanate by adding 25 cm³ of solution (a) to 25 cm³ of distilled water. With a dropper add 5 to 6 drops of 0.20 mol L⁻¹ iron (III) nitrate to the beaker and stir the solution. Now pour 0.5 cm³ of the resultant coloured solution into four petri dishes placed on a white surface (white paper)

Dish 1 is kept as reference for comparison. To dish 2 add two or three crystals of potassium thiocyanate and note the deepening of the colour near the crystals compared to the colour of the solution in dish 1. To dish 3 add three drops of iron (III) nitrate solution (b) and again note the intensification of colour compared to the colour of the solution in dish 1.

Any deepening of the red colour in dish 2 and dish 3 by addition of SCN^- or Fe^{3+} ions indicates that in dish 1 there was an equilibrium; not all the Fe^{3+} or SCN^- had been converted to $FeSCN^{2+}$. If the reaction had gone to completion towards the formation of $FeSCN^{2+}$, any further addition of Fe^{3+} or SCN^- would not have resulted in a change of colour. From this experiment we infer that

1   there exists a CHEMICAL EQUILIBRIUM

$$Fe^{3}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$
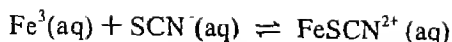
2   Addition of either Fe^{3+} or SCN^- leads to increase in the concentration of the $FeSCN^{2+}$ in the solution

Till now we have only seen the effect of increase in the concentration of Fe^{3+} or SCN^-. Is it possible to decrease the concentrations of either or both of these species? One way to reduce Fe^{3+} is to convert it by another reaction to a form which cannot react with SCN^-. This is achieved by adding (F^-) ions to the solution. In solution, Fe^{3+} reacts with F^- to form a series of colourless complex ions·

$$Fe^{3+}(aq) + F^-(aq) \longrightarrow FeF^{2+}(aq)$$

$$Fe^{3+}(aq) + 2F^-(aq) \longrightarrow FeF^{2+}(aq)$$
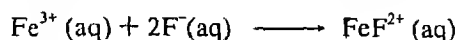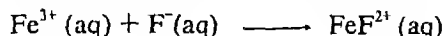
We now add to dish 4 match-head sized amounts of sodium fluoride and stir It will be noted that the colour of the solution in dish 4 has decreased in comparison to dish 1 As Fe^{3+} concentration is decreased, the $FeSCN^{2+}$ concentration decreases shifting the equilibrium to the left. Take 5 cm^3 of solution (d) in other dishes each time, and add $FeCl_3$, $Fe_2(SO_4)_3$, NH_4CNS and $NaCNS$ and confirm for yourself that the equilibrium we are studying concerns Fe^{3+} (aq) and SCN^- (aq) ions. The entire experiment may be repeated with combination of any one Fe (III) salt and any salt containing SCN^- as one of its ions.

We further infer

3   Decrease in the concentration of Fe^{3+} in a solution which has reached equilibrium, leads to a decrease in the concentration of $FeSCN^{2+}$.

In such reactions in solutions the rates are reasonably fast so that, to the eye, the changes look instantaneous. In reality, it takes a finite time to reach equilibrium, one can establish the time required by using modern sophisticated instruments It could also be shown using labelled radioactive reagents that the equilibrium is *dynamic* in the sense that *at equilibrium, the rate of forward reaction = rate of backward reaction and that such bidirectional conversions are taking place all the time.*

When we considered equilibria in physical changes, we were able to identify an expression involving concentration of the reactants, that remained constant with time, at a given temperature. Is there such an expression for chemical equilibria? If we had quantitatively determined the concentration of Fe^{3+}, SCN^- and $FeSCN^{2+}$ in our experiment in all the dishes, we would have established that after equilibrium was reached, the concentration ratio:

$$\frac{[FeSCN^{2+}]}{[SCN^-][Fe^{3+}]}$$

is a constant at a given temperature irrespective of the initial concentrations of Fe^{3+}

and SCN⁻, (here square brackets indicate concentration) In fact, our observation can be explained as follows:

In dish 2, when we added potassium thiocyanate crystals, we increased concentration of SCN⁻. This increase led to a readjustment, leading to an increase in $[FeSCN^{2+}]$ (and hence increase in red colour) and a consequent decrease in $[Fe^{3+}]$ and a new value for [SCN] so that

$$\frac{[FeSCN^{2+}]}{[SCN\ ][Fe^{3+}]}$$

reaches the same constant value as in dish 1. Similar increase in $[FeSCN^{2+}]$ results when we added Fe^{3+} in dish 3. In dish 4 when we reduced the concentration of $[Fe^{3+}]$ by the formation of complexes FeF^{2+} and FeF_2, the readjustment to maintain equilibrium demands decrease in $[FeSCN^{2+}]$ (leading to a decrease in the red colour) and a simultaneous increase in $[SCN^-]$ so that again we arrive at an equilibrium, where concentrations maintain the ratio.

$$\frac{[FeSCN^{2+}]}{[SCN^-][Fe^{3+}]}$$

to be the same constant as in dish 1.

Without further ado, we would generalise our experience with this experiment (many such experiments have been conducted over the years) and state what is known as the LAW OF EQUILIBRIUM

9.2.1 The Law of Equilibrium

From many experimental investigations it has been generalised that *at a particular temperature, for a chemical reaction given by*

$$aA + bB \rightleftharpoons xX + yY$$
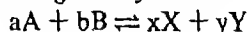
we have at equilibrium, the same value of the ratio

$$\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

i.e.

$$\frac{[X]^x[Y]^y}{[A]^a[B]^b} = K$$

where K is called THE EQUILIBRIUM CONSTANT.
The concentration ratio

$$\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

is denoted by Q (concentration quotient) and $Q = K$ *at equilibrium*. At equilibrium

which we know to be *dynamic* from experiments, especially with radioactive-labelled reactants, we infer that

Rate of forward reaction = Rate of backward reaction

After equilibrium is reached, when we change the concentration of any one of the reactants as we did in dishes 2 to 4, we change the concentration ratio Q. Then the concentrations will readjust themselves such that Q equals K, when equilibrium is reached *The law of equilibrium as expressed above was first studied by Guldberg and Waage in 1863.*

Example 9 3

Let us consider the following reactions and write the concentration quotient for them

a) CrO_4^{2-} (aq) + Pb^{2+} (aq) $\rightleftharpoons$ $PbCrO_4$ (s)

b) Fe^{3+} (aq) + SCN^- (aq) $\rightleftharpoons$ $FeSCN^{2+}$ (aq)

c) HCl (aq) $\rightleftharpoons$ H^+ (aq) + Cl^- (aq)

d) $CaCO_3$(s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

e) NH_3 (aq) + H_2O (l) $\rightleftharpoons$ NH_4^+ (aq) + OH^- (aq)

f) N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g)

Solution

We shall consider these examples in detail and explain various aspects involved in writing concentration quotient

Systems in 9 3 (a) and 9.3 (d) above are heterogeneous and the equilibria are heterogeneous equilibria here equilibria are between components in two different phases, namely, solid and liquid in (a) and solid and gas in (d)

We note that the quotient ratio and hence the equilibrium constant is defined in terms of the equation we write for the equilibrium
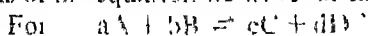
For $aA + bB \rightleftharpoons cC + dD$:

$$Q_1 = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

and for $cC + dD \rightleftharpoons aA + bB$

$$Q_2 = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Therefore, $Q_1 = \frac{1}{Q_2}$

In (a) $Q = \frac{[PbCrO_4 (s)]}{[CrO_4^{2-}][Pb^{2+}]}$

It is customary to assign for all solids, $[Solid] = 1$

$$[PbCrO_4 (s)] = 1$$

Again, by convention, $Q = \dfrac{1}{[CrO_4^{2-}][Pb^{2+}]}$

For (b) $Q = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$

For (c) $Q = \dfrac{[H^+][Cl^-]}{[HCl]}$

For (d) $Q = \dfrac{[CaO (s)][CO_2 (g)]}{[CaCO_3 (s)]}$

and by convention, $Q = [CO_2 (g)]$

In the concentration ratio of a reaction involving gas we can replace concen-
t .... ressure since at a given *temperature* the
f. .. .. oportional to its concentration.

$$Q_P = (p_{CO_2})$$

and at equilibrium $K = p_{CO_2}$ meaning that at equilibrium (closed system) the partial
pressure of CO_2 over solid $CaCO_3$ is a constant at a given temperature.

For (f)

we shall write $Q_P = \dfrac{(p_{NO_2})^2}{(p_{N_2O_4})}$

Strictly speaking, Q_P *defined in terms of partial pressures*, is not the same as Q_C
defined in terms of concentration. Since $c = p/RT$ for an ideal gas.

Q_P (in terms of pressure) $= Q_C$ (in terms of concentrations) $\times (RT)^n$
where n $=$ (sum of exponents in the numerator of Q)
     $-$ (sum of exponents in the denominator of Q)

When we consider   (e)

$$Q = \frac{[NH_4^+ (aq)][OH^- (aq)]}{[NH_3 (aq)][H_2O (l)]}$$

$$= \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} \quad \text{(written usually)}$$

Again by convention, H_2O is the solvent and is present in a *large* quantity and will not *appreciably* change during the reaction By convention, we treat the concentration of a solvent as constant and we write

$$Q' = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

In practice, the prime on Q is ignored and we write

$$Q = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

(that is, we put $[H_2O\ (l)] = 1$ by convention)

Our earlier discussion on the partial pressure of a liquid can be now reconciled as follows
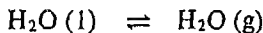
$$H_2O\ (l) \quad \rightleftharpoons \quad H_2O\ (g)$$

$$Q = \frac{[H_2O\ (g)]}{[H_2O\ (l)]}$$

$[H_2O\ (g)]$ is proportional to $p_{H_2O\ (g)}$ and by convention,
$$[H_2O\ (l)] = 1$$

Thus, the new constant, at equilibrium is

$$K = p_{H_2O\ (g)}$$

$p_{H_2O\ (g)}$ depends only on temperature and does not depend on the amount of liquid water present

9 2.2   The Magnitude of the Equilibrium Constant

The magnitude of the equilibrium constant, K, indicates how far a reaction can go; since for

$$aA + bB \quad \rightleftharpoons \quad cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where the concentrations are at equilibrium, it is obvious *that the larger the K, the greater will be the equilibrium concentration of the components on the right hand side of the reaction relative to those on the left hand side*

For example, in the system

$$Fe^{3+} (aq) + SCN^- (aq) \rightleftharpoons FeSCN^{2+} (aq,$$
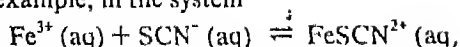
$$K = \frac{[FeSCN^{2+}]}{[SCN][Fe^{3+}]}$$

$$= 138 \text{ at } 298 \text{ K}$$

You may wonder why we have not written any unit for K. Defined in terms of concentrations, K has units. Strictly speaking, we cannot use concentration but a dimensionless quantity called ACTIVITY and in reality K derived from rigorous considerations is dimensionless. You will understand why it is dimensionless in your higher classes. We therefore, have given no units for K.

If $[FeSCN^{2+}] = 0.01$ mol L^{-1} at equilibrium and we started with equal concentration of Fe^{3+} and SCN we would find that at equilibrium

$[Fe^{3+}] = [SCN^-] = 0.0085$ mol L^{-1} only

Therefore, in practice the reaction has gone almost to completion.

For the reverse reaction

$$FeSCN^{2+} \rightleftharpoons Fe^{3+} + SCN^-$$
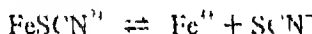
the equilibrium constant is (1/138) at 298 K and the small magnitude of K denotes that the reaction does not proceed much to the right.

Another example would be:

$$Cu (s) + 2Ag^+ (aq) \rightleftharpoons Cu^{2+} (aq) + 2Ag (s)$$
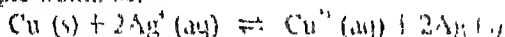
$$K = \frac{[Cu^{2+} (aq)]}{[Ag^+ (aq)]^2} = 2.0 \times 10^{15} \text{ at } 298 \text{ K}$$

and for $Cu (s) + Zn^{2+} (aq) \rightleftharpoons Cu^{2+} (aq) + Zn (s)$

$$K = \frac{[Cu^{2+} (aq)]}{[Zn^{2+} (aq)]} = 2.0 \times 10^{-19} \text{ at } 298 \text{ K}$$

By comparing the two K's we can conclude that while Ag will be precipitated by Cu when a copper rod is dipped in a solution containing Ag^+, Zn will not be precipitated by Cu when a copper rod is dipped in a Zn^{2+} solution. In fact the reverse is possible in the second case. When a Zn rod is dipped in a solution containing Cu^{2+} ion, Cu will be precipitated.

Example 9.4

Given that $K = 2.0 \times 10^{15}$ at 298 K for
    $Cu (s) + 2Ag^+ (aq) \rightleftharpoons Cu^{2+} (aq) + 2 Ag (s)$
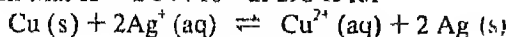
fill in the blanks in the following table for the three solutions at equilibrium

Solution	$[Cu^{2+}(aq)]$ mol L^{-1}	$[Ag^+(aq)]$ mol L^{-1}	$\dfrac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$
1.	(a)	1.0×10^{-9}	2.0×10^{15}
2	2.0×10^{-7}	1.0×10^{-11}	(b)
3.	2.0×10^{-2}	(c)	2.0×10^{15}

Solution

For the reaction, $Cu\ (s) + 2\ Ag^+\ (aq) \rightleftharpoons Cu^{2+}\ (aq) + 2\ Ag\ (s)$

$$K = \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$$

Substituting the values of concentration for Cu^{2+} (aq) and Ag^+ (aq), we get the values of

$$a = 2.0 \times 10^{-1} \text{ mol } L^{-1}$$
$$b = 2.0 \times 10^{15}$$
$$\text{and} \quad c = 3.16 \times 10^{-8} \text{ mol } L^{-1}$$

The table above states that there may be *at a given temperature,* many reaction mixtures, each having different concentrations, which are at equilibrium. However they obey the law of equilibrium

It must be obvious from our discussions that in the system described by

$$aA + bB \rightleftharpoons cC + dD$$
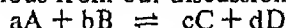
equilibrium would be reached whether the initial system starts with A and B or with C and D or for a matter of fact with any mixture of A, B, C and D, and at equilibrium our law of equilibrium has to be satisfied In the case of Cu^{2+}, Ag system, we can start with copper in a solution containing Ag^+ or with silver dipping in a solution containing Cu^{2+} or any combination of these, the systems will adjust towards equilibrium such that, at equilibrium

$$\frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2} = 2.0 \times 10^{15} \text{ at } 298 \text{ K}$$

The magnitude of the equilibrium constant depends on the equation written for a reaction The appropriate equation must be specified when an equilibrium constant is stated.

We could write

$$Fe^{3+}\ (aq) + SCN^-\ (aq) \rightleftharpoons FeSCN^{2+}\ (aq)$$
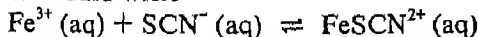
$$K_1 = \frac{[FeSCN^{2+}]}{[SCN^-][Fe^{3+}]}$$

$$= 138 \text{ at } 298 \text{ K}$$

We could have equally well written

$2 Fe^{3+} (aq) + 2 SCN^- (aq) \rightleftharpoons 2 Fe SCN^{2+}$
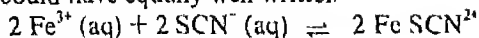
then, $K_2 = K_1^2$ at 298 K

Again:

$Cu (s) + 2Ag^+ (aq) \rightleftharpoons Cu^{2+} (aq) + 2Ag (s)$

$$K_1 = \frac{[Cu^{2+}(aq)]}{[Ag^+ (aq)]^2}$$

$$= 2 \times 10^{15} \text{ at 298 K}$$

Then, $1/2 Cu(s) + Ag^+ (aq) \rightleftharpoons 1/2 Cu^{2+} (aq) + Ag (s)$

$$K_2 = \frac{[Cu^{2+} (aq)]^{1/2}}{[Ag^+ (aq)]}$$

$$= K_1^{1/2} = (2 \times 10^{15})^{1/2}$$

$$= 4.5 \times 10^7 \text{ at 298K}$$

9.3 EFFECT OF CHANGING THE CONDITIONS OF SYSTEMS AT EQUILIBRIUM

If a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances then the system is no longer at equilibrium, net reaction will occur, until the system returns to equilibrium. We shall soon find that it is possible to predict the direction and magnitude of the change required to restore equilibrium. If the temperature of the system is changed suddenly, then the system will no longer be at equilibrium. The equilibrium constant depends upon temperature and a new equilibrium has to be established and we can again predict the direction and the extent of change that has to occur to attain equilibrium at the new temperature

9.3.1 Change of Concentration

In our experiment involving $Fe^{3+}(aq)$, $SCN^-(aq)$ and $FeSCN^{2+}(aq)$ (section 9.2), we observed that the addition of either Fe^{3+} or SCN^- increased the concentration of $FeSCN^{2+}$ (aq) as indicated by the darkening of the red colour. We also noted that when by the addition of sodium fluoride we decreased the concentration of Fe^{3+}, the red colour intensity decreased indicating a decrease in concentration of $FeSCN^{2+}$ These observations are consistent with a general law proposed towards the end of the nineteenth century by a French chemist Henry Louis Le Chatelier The general law is named the Le Chatelier's Principle and states: *If a system at equilibrium is subjected to a change which displace it from the equilibrium, a net reaction will*

$\vee$ ௬௫

occur in a direction that counteacts the change.

In the specific case where the concentration of a reactant is changed we can restate Le Chatelier's Principle: *If a system is at equilibrium and the concentration of one of the reactants is increased so that the system is no longer at equilibrium instantaneously, then the system will readjust so as to decrease the concentration of that reactant* .

We shall consider a few examples that illustrate this principle·

Clothes dry quicker when there is a breeze or when we keep shaking it. If an equilibrium is reached between the water in the cloth and the water vapour above it, a breeze or the act of shaking the cloth removes the water vapour from the immediate neighbourhood of the cloth; to re-establish the equilibrium more water molecules will have to escape from the cloth to the space above It is for the same reason that we sweat more on a humid day Since there is already considerable water in the atmosphere, water from the skin is unable to evaporate quickly. A fan helps by removing the water vapour from the area near the skin

The haemoglobin, 'Hb, in the red corpuscles of our blood carries oxygen to the tissues. The equilibrium to be considered is

$$Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$$
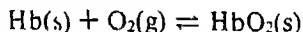
The blood that is equilibrated with the oxygen of the air in the lungs finds a situation in the tissues where partial pressure of oxygen is low and hence the equilibrium readjusts itself by some of the oxyhaemoglobin giving up the oxygen When the blood returns to the lungs the partial pressure of the oxygen is higher and more oxyhaemoglobin is formed.

Similarly the blood removes the carbon dioxide from the tissues. The equilibrium is

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
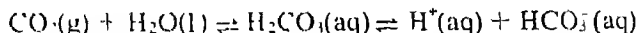
Here carbon dioxide dissolves in the blood in the tissues since partial pressure of carbon dioxide is high; in the lungs where the carbon dioxide partial pressure is low, it is released from the blood

In many manufacturing processes, the products formed are removed from the site of the reaction so that the equilibrium continuously readjusts itself towards the formation of the desired products. In the manufacture of ammonia by the Haber process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
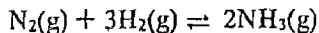
ammonia is continuously removed from the reaction site by liquefaction, so that more and more ammonia is formed by the system attempting to reach equilibrium.

When we want to precipitate metal ions by passing hydrogen sulphide we can selectively precipitate them by adding acid to the aqueous solution. The equilibrium is

$$Cu^{2+}(aq) + H_2S(aq) \rightleftharpoons CuS(s) + 2H^+(aq)$$

$$\text{and } Zn^{2+}(aq) + H_2S(aq) \rightleftharpoons ZnS(s) + 2H^+(aq)$$
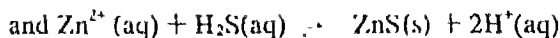
If the solution is made acidic, the increase in hydrogen ion concentration causes a net reaction in the direction

$$MS(s) + 2H^+(aq) \rightleftharpoons M^{2+}(aq) + H_2S(aq)$$
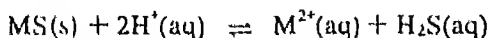
where M is Cu or Zn. This reaction leads to a dissolution of the sulphide. Since the equilibrium constants are different, ZnS dissolves in a slightly acidic medium whereas CuS does not. Thus we can separate the two ions by passing hydrogen sulphide through an acidified aqueous solution of the mixture of their ions

Change of Pressure in System Involving Gases· In systems involving a gaseous phase either in a homogeneous or heterogeneous system, the pressures of the gases play a dominant role since increase in partial pressure increases the concentration of the species in the gaseous phase.

Consider the equilibrium:

$$CO_2(g) + H_2O(l) \rightleftharpoons CO_2(aq)$$
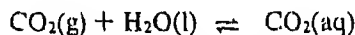
Increasing the partial pressure of $CO_2(g)$ should lead to increased solubility according to Le Chatelier's principle. [The partial pressure of $CO_2(g)$ will be lowered only if $CO_2(g)$ dissolves in water to form $CO_2(aq)$].

When we have a homogeneous gaseous system, such as in the Haber process of manufacture of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
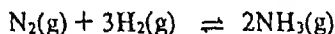
increase in total pressure would lead to more ammonia being formed. Since the number of molecules on the right-hand side is smaller than that on the left-hand side, an increase in pressure can be offset by a decrease in the total number of molecules. According to Le/Chatelier's/principle, the equilibrium will shift towards the right to decrease the number of molecules An increase of total pressure (say, by compression) increases the partial pressures of all the components by the same ratio and this will have effect only if there is a net change in the total number of molecules in the reaction considered. A compression leads to a decrease in volume at a constant temperature. Le Chatelier's principle for systems involving gases can be stated as.

1. *If a system is at equilibrium and the partial pressure of one of the reactants in the gas phase is increased, then the system will readjust to decrease the partial pressure of that reactant.*

2. *When the total pressure is increased in a homegenous case then the system will react in such a way as to decrease the total number of molecules.*

9 3.2 Change of Temperature

The equilibrium constant changes when temperature is changed By Le Chatelier's principle we can predict that *when temperature is increased the system will react such that the increase* ~ k ~ ... *: ." C 7 : : ... tent. Therefore, increase of temper* ~ ... : : ·· .. .,:. .. .·· · :.. .: Tion *which is endothermic.* Therefore, for an equilibrium which is exothermic as written, the equilibrium constant will decrease with increase of temperature

Let us consider the direction in which solubility in water of the following substances will change with temperature. NH_4Cl, $CaCl_2$, $NaCl$, $NaNO_3$. For NH_4Cl and $NaNO_3$ heat is absorbed, for $CaCl_2$ heat is evolved and for $NaCl$ there is very little heat change

Using Le Chatelier's principle, we can predict that the solubility of NH_4Cl and $NaNO_3$ will increase with temperature, that of $CaCl_2$ will decrease with increase of temperature, the solubility of $NaCl$ will be almost independent of temperature.

Again in the Haber's process of manufacture of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = - 92 4 kJ$$
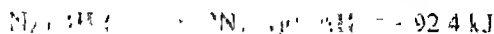
increase of temperature decreases the yield of ammonia, as predicted by Le Chatelier's principle, even though the rate at which equilibrium is attained increases with temperature as we shall see in unit 11

... ?Her ... Δ d g/pi

It important to realise that the potential that governs equilibrium is free energy change at constant ... and pressure, $\Delta G_{T,P} = 0$ at equilibrium.

This is to mean that at equilibrium the total free energy of the reactants on the left hand side is equal to the total free energy of the reactants on the right hand side of the equation.

$$A + B \rightleftharpoons C + D$$

It should be emphasised that we have not discussed anywhere how quickly the equilibrium is reached when we mix, let us say A and B All that we said was that at equilibrium, the rate of formation of C and D from A and B is equal to the rate of formation of A and B from C and D. If these rates are very fast then the equilibrium will be reached quickly. If the rates are very slow then the equilibrium will be reached slowly. In Unit 11 we shall discuss rates of reactions.

If we mix $H_2(g)$ and $O_2(g)$, water is not formed unless a catalyst is used or we subject the mixture to heat from a flame or to an electrical discharge. It is well known that for

$$H_2(g) + O_2(g) \rightleftharpoons H_2O(g)$$
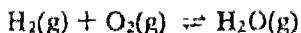
the equilibrium constant is 1.2×10^{40} at 298 K and the equilibrium when reached is far to the right, because K is very large. Under normal conditions, the equilibrium is never reached when you mix $H_2(g)$ and $O_2(g)$. However, in the presence of a catalyst such as platinised asbestos the reaction proceeds very fast. The question is whether the catalyst can change the equilibrium constant The answer is a definite NO, since the equilibrium depends only on the free energy difference between the left-hand side reactants and the right-hand side reactants and is independent of the speed with which equilibrium is attained What a catalyst does is to speed up the reaction, both the forward and the backward reactions.

Catalysts play an important role in life processes as well as in industries. We shall discuss them in Unit 11. In the Haber process of manufacture of ammonia, besides using high temperature and high pressure, an iron catalyst is used to increase the yield. The increase in yield is not due to change in the equilibrium constant. In the process ammonia is actually removed from the reaction site by liquefaction, and the presence of a catalyst ensures that the system reacts quickly to drive the reaction

$$2N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
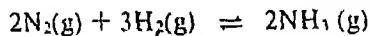
to the right-hand side in its effort to attain equilibrium when the ammonia concentration is being constantly depleted.

9.4 EQUILIBRIA INVOLVING IONS

Chemical reactions in solutions, especially aqueous solutions, play an important role in chemistry. Water is a solvent which separates the ions that form an ionic bond. For example, sodium chloride when dissolved in water makes water a good conductor of electricity Water has a special property that enables Na^+ and Cl^- ions, forming an ionic bond in sodium chloride crystal, to separate and be free enough to carry electrical charges between the electrodes Solvents like water which allow charge to separate are called POLAR SOLVENTS In fact the solubility of sodium chloride in water arises from this ability of water to separate its ions. In contrast, we have other solvents such as kerosene in which sodium chloride would dissolve only sparingly. However, naphthalene (moth balls) which is a covalent compound would dissolve easily in kerosene. Kerosene and like solvents are known as NON-POLAR SOLVENTS.

Let us test the solubility of the following in kerosene and water.

a) Sugar
b) Kerosene
c) Tar
d) Grease
e) Ammonium chloride

f) Manganese dioxide
g) Lead chromate
h) Barium chloride
i) Barium sulphate
j) Ethyl alcohol

You will realise that there are classes of substances which dissolve only in water, some dissolve only in kerosene, a few dissolve in both and a few that do not seem to dissolve in either In fact what we mean here by not soluble is a qualitative estimate, it is better to say sparingly soluble rather than insoluble

In chemistry we deal with a large number of reactions in aqueous solutions involving chemicals which are ionic in nature. Much of analytical chemistry is carried out in aqueous solutions. We will now discuss how the concepts of chemical equilibria we have discussed till now, could apply to solutions when ions are present. In discussing the reaction between Fe^{3+} and SCN^-, we had implicitly assumed that in water we have these ionic species. (It is also known that in most ionic reactions equilibrium is reached very quickly)

9 4.1 Ionisation of Electrolytes

Ions in solution arise in two ways· (i) the solute is a truly ionic compound or salt, so that the ions which already exist in the solid, separate more freely in solution, or (ii) the solute is a polar covalent compound that reacts with the solvent (for example water) to form ions. In fact, this breaking of compounds in solution into ions is *ionisation.* The extent to which a compound ionises is called the degree of ionisation. The compounds which give ions in aqueous solutions are electrolytes

Truly ionic substances are strong electrolytes. For example, NaCl, KBr, NH₄Cl, KCl, NaOH When 1 mole KCl is added to 1 litre of water, the resulting solution essentially contains 1.0 mole of K^+ and 1.0 mole of Cl^- ions and no unionised KCl. No doubt, these ions are not free particles. They are solvated ions $K^+(aq)$ and Cl^- (aq). However, in case (ii) of polar covalent compounds a solute may be a strong or weak electrolyte depending on the degree of ionisation You might be aware of acids hydrochloric acid (HCl), nitric acid (HNO₃) and sulphuric acid (H₂SO₄). Their aqueous solutions are essentially 100% ionised. There are only a few unionised molecules present at equilibrium. Therefore, equations for the ionisation reactions are written with only a single arrow directed to the right.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$
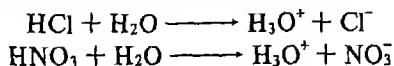
On the other hand, acetic acid, CH₃COOH and ammonia, NH₃ are weak electrolytes. Their aqueous solutions are weakly ionised.

In such cases, molecules of the electrolyte are in equilibrium with its ions. Ionisation of such electrolytes is written with double arrows ($\rightleftharpoons$)

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
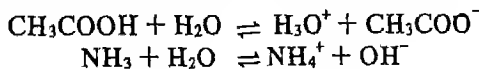
As ionisation of strong electrolytes such as HCl and NaOH, is practically complete, there will not be much gain in studying this type of reaction from the

equilibrium point of view. Equilibria involving weak electrolytes where there is only partial ionisation are of great importance.

Ionisation of Weak Electrolytes: Weak electrolytes are partially ionised in water solution. Dissolved molecules exist in equilibrium with their ions in such solutions. The following chemical equation represents ionisation of weak acid, acetic acid, in water solution.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
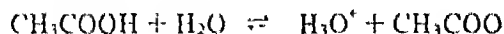
Equilibrium constant, K will be written as

$$K = \frac{[H_3O^+][CH_3COO^-]}{[H_2O][CH_3COOH]}$$

As discussed earlier, we write $[H_2O] = 1$.

We obtain

$$K_a = K[H_2O] = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Equilibrium constant, K_a is *acid ionisation constant* or *acid dissociation constant*. $[H_3O^+]$ is called the hydronium ion. Earlier, it was customary to write:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

This practice has been given up since H^+ exists only as H_3O^+ and dissociation arises only from a transfer of H^+ to a proton acceptor, water.

The degree of ionisation, α, of a weak electrolyte in water solution is the fraction of the total concentration of the electrolyte, that is, in ionic form at equilibrium. The degree of ionisation of weak electrolyte is related to K_a. Let us take the example of acetic acid. According to the chemical equation, for every mole of CH_3COOH ionised, one mole of CH_3COO^- and one mole of H_3O^+ must form. Suppose the concentration of CH_3COOH initially present is c mol L^{-1} and only a fraction say, α, of this amount, is ionised. Then, at equilibrium, the concentrations of the three species would be as follows:

$$[CH_3COO^-] = c\,\alpha, \quad [CH_3COOH] = c\,(1-\alpha)$$
$$[H_3O^+] = c\,\alpha$$

Therefore, $K_a = \dfrac{c\,\alpha^2}{(1-\alpha)}$

If α is very small compared to 1, the value of α can be neglected in the denominator. The expression of K_a then becomes

$$K_a = c\,\alpha^2$$

The degree of ionisation, α, can be calculated at any concentration c, if the value of K_a is known Thus

$$\alpha = (K_a/\, c)^{1/n}$$

The following examples will illustrate the methods.

Example 9 5

Calculate the degree of ionisation and $[H_3O^+]$ of a 0.01 mol L^{-1} CH_3COOH solution. The acid dissociation constant of acetic acid is $1\,8 \times 10^{-5}$

Solution

For the reaction

$$CH_3COOH\ (aq) + H_2O(l)\ \rightleftharpoons\ H_3O^+(aq) + CH_3COO^-(aq)$$
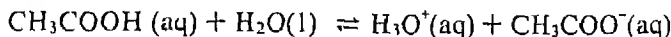
Let α be the degree of ionisation, then the concentrations of various species in solution at equilibrium will be

$$[H_3O^+] = 0.01\ \alpha$$
$$[CH_3COO^-] = 0\,01\ \alpha$$
$$[CH_3COOH] = 0.01\ (1-\alpha)$$

$$K_a = \frac{0.01\,\alpha \times 0.01\,\alpha}{0\,01(1-\alpha)}\ =\ \frac{(0\,01)\alpha^2}{(1-\alpha)}$$

Assuming α to be small compared to 1

$$K_a\ =\ 1.8 \times 10^{-5} = 0.01\ \alpha^2$$

Therefore
$$\alpha^2\ =\ 1.8 \times 10^{-3}$$

or
$$\alpha\ =\ 4.24 \times 10^{-2}$$
$$[H_3O^+] =\ c\ \alpha = 0\,01 \times 4\,24 \times 10^{-2}\ \text{mol}\ L^{-1}$$
$$=\ 4.24 \times 10^{-4}\ \text{mol}\ L^{-1}$$

Example 9.6

At 298K, a 0 1 M solution of acetic acid is 1.34% ionised What is the ionisation constant, K_a, for acetic acid ?

Solution

Let us assume that we have 1 litre of solution. Since the acid is only 1 34% ionised, the number of moles of CH_3COOH in ionic form is

$$(0\,0134)\ (0.1\ \text{mol of}\ CH_3COOH) = 0.00134\ \text{mol of}\ CH_3COOH$$

The number of moles of unionised (molecular form) acetic acid

$$=\ (0\,1 - 0.00134)\ \text{mol} = 0.0987\ \text{mol}$$

According to the chemical equation, $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$, 1 mol of H_3O^+ and 1 mol of CH_3COO^- are produced for every mole of CH_3COOH that ionises. Therefore, 0 00134 mol L^{-1} ionised acetic acid will give 0 00134 mol L^{-1} of H_3O^+ ion and 0 00134 mol L^{-1} CH_3COO^- ion.

Concentrations at equilibrium are,

$$H_2O \;+\; CH_3COOH \rightleftharpoons H_3O^+ \;+\; CH_3COO^-$$

$$\begin{array}{ccc} & 0\,0987 & 0\,00134 \quad 0.00134 \\ & \text{mol L}^{-1} & \text{mol L}^{-1} \quad \text{mol L}^{-1} \end{array}$$
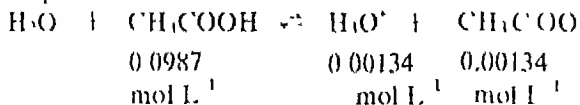
Thus, K_a can be obtained using equilibrium concentrations.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[0\,00134][0.00134]}{[0\,0987]}$$

$$1\,82 \times 10^{-5}$$

9.4.2   Acid-Base Equilibrium

According to the early views of chemists, acids were substances that tasted sour, changed the colour of litmus from blue to red, reacted with certain metals to give off hydrogen gas, formed carbon dioxide with carbonates and, above all, were able to neutralise bases. Bases (originally called alkalis) were substances that tasted bitter, felt slippery, changed the colour of litmus from red to blue and, above all, were able to neutralise acids.

In 1884, S Arrhenius, as a part of his theory of ionisation, proposed a new theory of acids and bases. According to Arrhenius' theory acids were substances that produced hydrogen ions (H$^+$) when mixed with water, bases were substances that produced hydroxyl ions (OH$^-$) when mixed with water. According to this theory neutralisation of acids and bases is basically a reaction between H$^+$ and OH$^-$ ions.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$
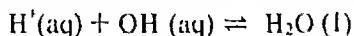
Arrhenius theory was a good beginning for acids and bases.

Bronsted-Lowry Theory   The Arrhenius theory of acids and bases was further extended by Johannes Bronsted and Thomas Lowry in 1923. They proposed a more general concept of acids and bases. According to the Bronsted-Lowry theory *an acid is a proton donor* while *a base is a proton acceptor*. The advantage of this theory is that the definition of an acid or a base is not restricted to neutral molecules. Let us illustrate this by the following example

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$
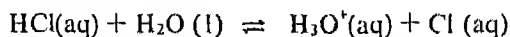
In this example, HCl donates its one proton to become Cl^- and H_2O accepts one proton to become H_3O^+. Thus HCl is an acid and H_2O is a base. Here, H_3O^+ is having a proton and can give it again, therefore according to the Bronsted theory

H_3O^+ is an acid. Similarly, HCl, having lost the proton, has become Cl^- and this Cl^- can take the proton back, therefore it is a base. Thus donating protons is a reversible process Every acid must form a base on donating its proton, and every base must form an acid on accepting a proton. The above reaction can be written as

$$HCl(aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

| acid 1 | base 2 | acid 2 | base 1 |
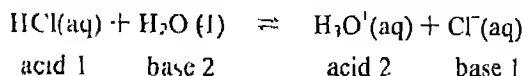
The base that results when an acid donates its proton is called the CONJUGATE BASE of the acid Correspondingly, the acid that results when a base accepts a proton is called the _conjugate acid_ of the base. In the reaction mentioned above, Cl^- is the conjugate base of the acid HCl and H_2O is the conjugate base of the acid H_3O^+. Thus, the conjugate acid differs from its conjugate base by one proton The following equations provide specific examples of conjugate acid-base pairs

Acid 1	+	Base 2	$\rightleftharpoons$	Acid 2	+	Base 1
H_2O (l)	+	$NH_3(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
$HCl(aq)$	+	$NH_3(aq)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$Cl^-(aq)$
$NH_4^+(aq)$	+	$CH_3COO^-(aq)$	$\rightleftharpoons$	$CH_3COOH(aq)$	+	$NH_3(aq)$
$H_2O(l)$	+	$CO_3^{2-}(aq)$	$\rightleftharpoons$	$HCO_3^-(aq)$	+	OH^-
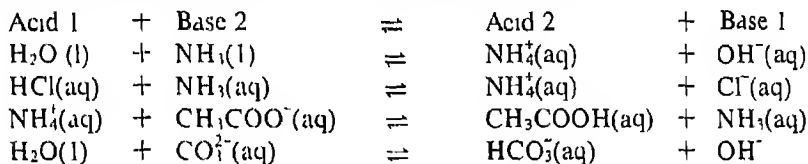
Certain acids can give up two or three protons These are called diprotic (for example, H_2SO_4) or triprotic (for example, H_3PO_4) acids, respectively According to the Bronsted concept each acid is regarded as giving up only one proton Such acids (diprotic and triprotic) give out protons in different steps

There are certain substances which can act as acids as well as bases and they are called amphoteric

Acid 1		Base 2	$\rightleftharpoons$	Acid 2		Base 1
$HCl(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	Cl^-
$H_2O(l)$	+	$NH_3(aq)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
$HCO_3^-(aq)$	+	$NH_3(aq)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$CO_3^{2-}(aq)$
$HCl(aq)$	+	$HCO_3^-(aq)$	$\rightleftharpoons$	$H_2CO_3(aq)$	+	$Cl^-(aq)$
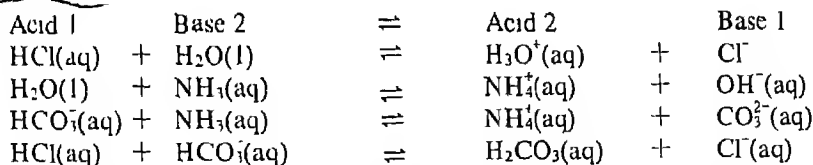
Strengths of Acids and Bases· According to Bronsted–Lowry an acid is a proton donor and base is a proton acceptor Therefore, the strength of an acid or a base is determined by its tendency to lose or gain protons A strong acid is a substance which loses a proton easily to a base. The conjugate base of a strong acid is a weak base

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + Cl^- (aq)$$

| strong acid | weak base |
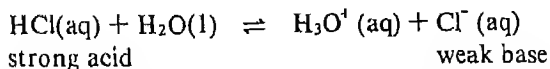
Here chloride ion, Cl^-, the conjugate base of hydrogen chloride, shows little tendency to react with proton in water solution to form hydrogen chloride molecules,

hence it is a weak base. Conversely, the conjugate base of a weak acid is a strong base,

$$CH_3COOH (aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + CH_3COO^- (aq)$$
weak acid   strong base
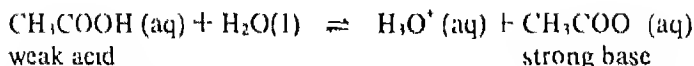
The conjugate base CH_3COO^- (aq) of weak acid CH_3COOH shows a very strong attraction for a proton and is therefore a strong base.

A strong base has a high tendency to accept protons. Therefore, *the conjugate acid of a strong base is a weak acid* and conversely, *the conjugate acid of a weak base is a strong acid.*

$$CH_3COO^-(aq) + H_3O(aq) \rightleftharpoons CH_3COOH(aq) + H_2O(l)$$
strong base   weak acid
$$Cl^- (aq) + H_3O^+(aq) \rightleftharpoons HCl (aq) + H_2O(l)$$
weak base   strong acid
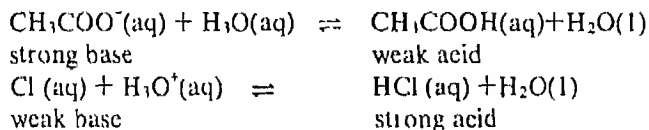
The ability of an acid to lose a proton (acid strength) is experimentally measured by its acid *ionisation constant.* The larger the value of the acid ionisation constant K_a the higher is the concentration of H_3O^+ and the stronger the acid. We can talk of relative strengths o   their ionisation constants at a particular temperature.

The ionisation constant of acetic acid, K_a is written as

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \text{ at } 298K$$

and of HF is written as

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.7 \times 10^{-4}$$

Since the ionisation constant of HF is larger than the ionisation constant of CH_3COOH, hydrofluoric acid ionises in water to a greater extent and is a stronger acid than acetic acid.

The general principle employed to compare strength of acids is also used to compare the strength of bases. The bases, ammonia and hydroxide ion, can compete for a proton

$$NH_3 + H-OH \rightleftharpoons NH_4^+ + OH^-$$
base 1   acid 2   acid 1   base 2
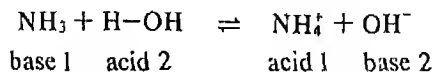
Similar to acid ionisation constant, base ionisation constant can be written as

$$K_{base} = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.76 \times 10^{-5}$$

The small value of K_b indicates that formation of OH^- is not favoured. This

indicates ammonia is a weaker base than OH

Example 9 7

Calculate the concentration of H_3O^+ ion in a mixture of 0.02 M of acetic acid and 0 1 M sodium acetate. Ionisation constant for acetic acid is $1 8 \times 10^{-5}$.

Solution

Acetic acid is a weak electrolyte and ionises weakly whereas sodium acetate is a strong electrolyte and therefore ionises strongly in solution

Let x mole of acetic acid be ionised Then the concentration of various ions can be written as follows:

$$CH_3COOH (aq) + H_2O \ \rightleftharpoons \ H_3O^+(aq) + CH_3COO^- (aq)$$
$$(0.02 - x) \qquad\qquad\qquad x$$

$$CH_3COONa \ \rightleftharpoons \ Na^+(aq) + CH_3COO^- (aq)$$
$$0.1 \qquad\qquad 0.1$$
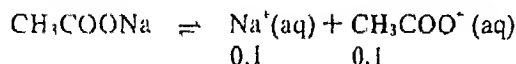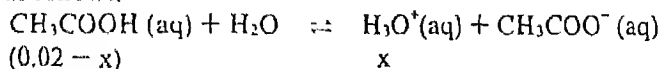
As x is small as compared to 0.1,

$$[CH_3COO^-] = 0.1 + x \simeq 0.01 \ \text{mol L}^{-1}$$

and
$$[CH_3COOH] = 0.02 - x \simeq 0.02 \ \text{mol L}^{-1}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$
$$= x \times \frac{0 1}{0.02} = 1.8 \times 10^{-5}$$

$$[H_3O^+] = x = 3.6 \times 10^{-6} \ \text{mol L}^{-1}$$

Lewis acid-base concept: Lewis gave a broad definition of acids and bases. Lewis defined *bases as species (charged or uncharged) which can donate an electron pair,* *and acids as species (charged or uncharged) which can accept an electron pair* These definitions of acids and bases fit the Bronsted-Lowry and Arrhenius theories, as well as many other substances which could not be explained as acids or bases in terms of proton transfer. A reaction between ammonia and boron trifluoride can be seen as an acid-base reaction.

$$H_3N: \quad + \quad BF_3. \quad \longrightarrow \quad H_3N{\rightarrow}BF_3$$
$$\text{base} \qquad\quad \text{acid} \qquad\qquad\quad \text{product}$$
$$\text{(Ammonia)} \quad \text{(boron trifluoride)} \quad \text{(ammonia-boron trifluoride)} \cdot$$
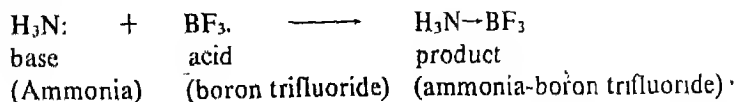
According to Lewis' definition, a hydroxide ion, OH^- and water molecule, H_2O, are Lewis bases since each of them can donate a pair of electrons to proton

$$H^+ \quad + \quad OH^- \rightarrow H{:}O{-}H$$
$$\text{acid} \qquad \text{base}$$

$$H^+ + \cdot O - H \; \rightleftharpoons \; [H \; O - H]^+$$

$$\quad\quad\quad H \quad\quad\quad\quad\quad H$$

acid   base
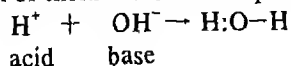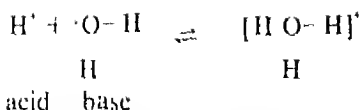
A metal ion can also behave like a Lewis acid —

$$2H_3N: + Ag^+ \longrightarrow [H_3N \cdot Ag \cdot NH_3]^+$$

base   acid
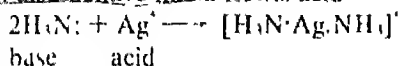
9 4.3   Ionisation of Water

We have seen that water is amphoteric in nature. However, even if no acid or base is added, there is still some H_3O^+ and OH^- present in pure water. Some of the water molecules react with each other, one molecule of water acting as an acid, another as a base, to produce OH^- and H_3O^+.

$$H_2O(l) + H_2O(l) \; \rightleftharpoons \; H_3O^+(aq) + OH^-(aq)$$

acid   base   acid   base

The equilibrium constant for this reaction is,

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

With our usual convention, $[H_2O] = 1$ and thus

$$K [H_2O]^2 \quad K_w = [H_3O^+][OH^-]$$

The constant, K_w, is given the name IONIC PRODUCT OF WATER. At 298 K,

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}$$

At temperatures other than 298 K, the H_3O^+ and OH^- concentrations are equal but the values of K_w are different from that at 298 K. For example, at 323 K, $K_w = 5.48 \times 10^{-14}$. Therefore, $[H_3O^+] = [OH^-] = 2.34 \times 10^{-7}$ mol L^{-1}.

The addition of an acid, such as HCl, or a base such as NaOH changes the concentrations of H_3O^+ and OH^- ions so that they are not equal. However, the product, $[H_3O^+][OH^-]$ must remain equal to K_w. Therefore, when an acid is added, the $[H_3O^+]$ is increased and hence $[OH^-]$ must decrease. On the other hand when a base is added to water, then $[OH^-]$ increases and hence the $[H_3O^+]$ decreases.

Example 9.8

(a) The $[OH^-]$ of a water solution is 10^{-5} mol L^{-1}. What is the $[H_3O^+]$?

(b) The $[H_3O^+]$ of a water solution is 4.3×10^{-2} mol L^{-1}. What is the $[OH^-]$?

Solution

(a) $K_w = [H_3O^+][OH^-] = 10^{-14}$

$$[H_3O^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9} \text{ mol } L^{-1}$$

(b) $K_w = [H_3O^+][OH^-] = [4 3 \times 10^{-3}][OH^-] = 10^{-14}$

$$[OH^-] = \frac{10^{-11}}{4 3 \times 10^{-2}}$$

$$= 2.3 \times 10^{-11} \text{ mol L}^{-1}$$

pH-Value The hydronium ion concentration $[H_3O^+]$ is a significant quantity in every biological process and in many industrial processes It is possible to describe quantita-tively the acidic or basic character of an aqueous solution by specifying the concentration of $[H_3O^+]$ For example, a solution with $[H_3O^+] = 5 \times 10^{-3}$ mol L^{-1} is more acidic and less basic than one in which $[H_3O^+]$ is 6×10^{-4} mol L^{-1} For the purpose of convenience, Sorensen in 1909 defined a new scale called the pH scale. *pH* is defined as the negative logarithm (base 10) of the $[H_3O^+]$ concentration in moles per litre.

$$\boxed{pH = -\log_{10}[H_3O]^+} = (\log 10^{-7} \approx \log 10^{-7} \cdot (-7)$$

It is very easy to convert $[H_3O^+]$ to pH, and vice versa At 298 K in a neutral solution,

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

Therefore,

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[1 0 \times 10^{-7}] = 7$$

When the pH is above 7, the solution is basic (alkaline) and when it is below 7, the solution is acidic. The lower the pH, the higher the H_3O^+ concentration For example, the pH of a solution containing H_3O^+ concentration $= 1 \times 10^{-2}$ mol L^{-1} will be 2, but that of a solution containing lower concentration of hydronium ion, $[H_3O^+] = 1.0 \times 10^{-6}$ mol L^{-1}, pH will be 6.

Example 9 9

What is the pH of a solution whose hydronium ion concentration is 6.2×10^{-9} mol L^{-1}?

Solution

$$pH = -\log[H_3O^+]$$
$$= -\log[6 2 \times 10^{-9}]$$
$$= -(\log 6.2 + \log 10^{-9})$$

The value of log 6.2 = 0 79, and log 10^{-9} = 9

Therefore, $pH = -(0 79 - 9) = -(-8.21)$
$$= 8 21$$

Example 9.10

Calculate $[H_3O^+]$ and $[OH^-]$ of an alcoholic beverage which has pH = 4 70.

---

* The symbol pH derived from *Potenz*, the Danish word for power, is an abbreviation of 'power of hydrogen ion'

Solution

$$pH = -\log [H_3O^+] = 4.70$$
$$\log [H_3O^+] = -4.70 = -5 + 0.3$$

Taking antilog we get

$$[H_3O^+] = 10^{-5} \times 2.0$$
$$= 2.0 \times 10^{-5} \text{ mol l.}^{-1}$$

As we know,

$$K_w = [H_3O^+][OH^-]$$
$$1.0 \times 10^{-14} = 2.0 \times 10^{-5} \times [OH^-]$$
$$\text{Therefore, } [OH^-] = 5 \times 10^{-10} \text{ mol l.}^{-1}$$

The concentrations of H_3O^+ and OH^- are 2.0×10^{-5} and 5.0×10^{-10} mol L^{-1} respectively.

Example 9.11

Calculate the $[H_3O^+]$ and $[OH^-]$ and pH of a 0.2 M solution of hydrocyanic acid, HCN. Ionisation constant of HCN at 298 K is 7.2×10^{-10}

Solution

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$
$$K_a = 7.2 \times 10^{-10}$$
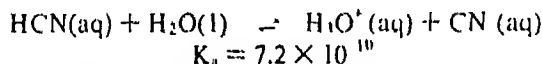
If x mole of HCN is ionised, then that will give x mole of H_3O^+ and x mole of CN^-. (0.2−x) mole of HCN will remain unionised, therefore,

$$K_a = \frac{x.x}{(0.2-x)} = \frac{x^2}{(0.2-x)} = 7.2 \times 10^{-10}$$

Assuming x to be very small, $\frac{x^2}{0.2} = 7.2 \times 10^{-10}$ or $x = 1.2 \times 10^{-5}$

Therefore,

$$[H_3O^+] = [CN^-] = 1.2 \times 10^{-5} \text{ mol } L^{-1}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.3 \times 10^{-10} \text{ mol } L^{-1}$$

Thus, $pH = -\log(1.2 \times 10^{-5}) = 4.92$

9.4.4 Solubility Product

Most substances dissolve in water at least to some extent. There are some substances whose solubility in water is so small that they are called 'insoluble' or 'sparingly soluble'. For example, AgCl, $BaSO_4$, AgBr, ZnS, etc.

When a saturated solution of a sparingly soluble salt is in contact with undissolved salt (at a constant temperature), an equilibrium is established when the rate of dissolution of ions from the solid equals the rate of precipitation of ions from the saturated solution. Suppose we have taken silver chloride, then, an equilibrium

exists between the solid silver chloride and a saturated solution of silver chloride. (Since solubility of silver chloride is extremely low, therefore whatever silver chloride dissolves will ionise completely).

$$\text{Undissolved salt} \rightleftharpoons \text{ions in solution}$$
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
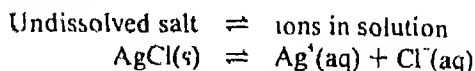
Like any other equilibrium constant, K for sparingly soluble salts may be calculated from equilibrium concentrations expressed in mol L^{-1}.

$$\text{Thus,} \qquad K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

By convention, $[AgCl(s)] = 1$, AgCl is a solid.
We can combine K with $[AgCl(s)]$ and get another constant,

$$K[AgCl(s)] = [Ag^+][Cl^-] = K_{sp}$$
$$\boxed{K_{sp} = [Ag^+][Cl^-]} \quad \subseteq P$$

The constant K_{sp} is known as the SOLUBILITY PRODUCT
The solubility product expression for

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
$$K_{sp} = [Pb^{2+}][Cl^-]^2$$
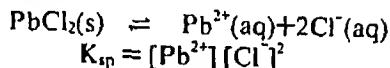
For $Ca_3(PO_4)_2$ equilibrium,

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$
$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$
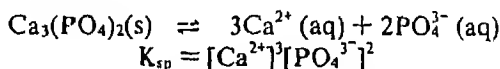
The solubility product of a substance can be calculated if its solubility is known and vice versa. Since the solubility of a substance changes with temperature, K_{sp} changes with temperature

Example 9.12
At 298 K, the solubility of silver chloride in water is 0 00138 g L^{-1}. What is K_{sp}?

Solution

$$\text{Molar solubility of AgCl} = \frac{0.00138 \text{ g AgCl}}{1 \text{ L}} \times \frac{1 \text{ mol AgCl}}{143 \text{g AgCl}}$$
$$= 1.31 \times 10^{-5} \text{ mol } L^{-1}$$

For each mole of AgCl dissolving, 1 mol of Ag^+ and 1 mol of Cl^- are formed.
$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
$$1.31 \times 10^{-5} M \quad 1.31 \times 10^{-5} M$$
$$K_{sp} = [Ag^+][Cl^-]$$
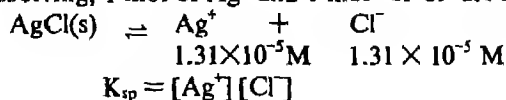
$$= (1.31 \times 10^{-5})^2$$
$$= 1.7 \times 10^{-10}$$

TABLE 11.1

Solubility Product (Ksp) of a Few Sparingly Soluble Salts at 298K

Compound	Ksp	Compound	Ksp
AgCl	1.7×10^{-10}	PbSO$_4$*	1.06×10^{-8}
AgBr	7.7×10^{-13}	SrSO$_4$*	3.8×10^{-7}
AgI	1.5×10^{-16}	Zn(OH)$_2$	1×10^{-17}
BaCO$_3$	8.1×10^{-9}	ZnS*	1.2×10^{-23}
BaSO$_4$	1.08×10^{-10}		
CaF*	3.4×10^{-11}		
CuS*	8.5×10^{-45}		
HgS	1×10^{-52}		
PbCl$_2$	1.7×10^{-5}		

* Solubility product is taken at 291K

The knowledge of solubility product is of great importance in various industrial and analytical processes. The precipitation of a salt occurs only when the product of ionic concentrations exceeds the solubility product at a particular temperature

In qualitative analysis, the separation and identification of metal ions, such as Cu^{2+}, Zn^{2+}, etc. as sulphides is possible only due to the differences in the solubility products of their sulphides.

EXERCISES

9.1   Can equilibrium be achieved between water and its vapour in an open vessel? Explain your answer and say what happens eventually.

9.2   A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
       (i)   What is the initial effect of the change on the vapour pressure?
       (ii) How do the rates of evaporation and condensation change initially?
       (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

9.3 A vessel has two compartments connec-
ted at the top (see Figure along side)
In one compartment (B) radioactive
methyl iodide* (CH_3I) is placed and in
the other (A) normal methyl iodide is
placed Will the vapour over A and B
become radioactive? Will the radioacti-
vity spread to the liquid in compart-
ment A Discuss in terms of the dyna-
mic nature of the equilibrium between
the vapour and its liquid
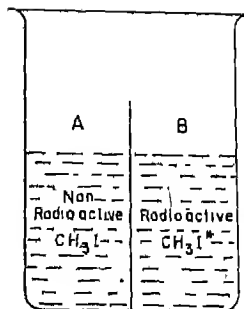
9,4 Fill in the blanks in the following table which lists the solubility data of oxygen in
water at 299 K

O_2 pressure (kPa)	$[O_2(g)]eq$ (mol L^{-1})	$[O_2(aq)]$ eq (mol L^{-1})	$\dfrac{[O_2(aq)]eq}{[O_2(g)]eq}$
106 4		0 012	—
	0 080	—	0 029
333.3	0 13	—	0.029
466.1		0.0053	—
598.8	·	—	0.028

9 5 Write the equilibrium constant expression for the following reactions·
  (i) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$
  (ii) $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$
  (iii) $CH_3COCH_3(l) \rightleftharpoons CH_3COCH_3(g)$
  (iv) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$
  (v) $Al(s) + 3H^+(aq) \rightleftharpoons Al^{3+}(aq) + 3/2H_2(g)$
  (vi) $HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$
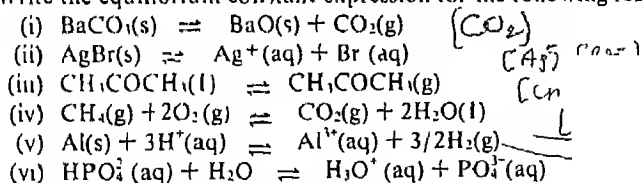
9 6 At 700 K, the equilibrium constant, K_p, for the reaction
  $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
  is (1.80×10^{-3}kPa) What is the numerical value in moles per litre of K_c for this
  reaction at the same temperature?
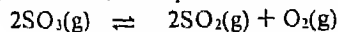
9.7 Bromine water (a dilute solution of bromine in water) is brown and weakly acidic
because of the equilibrium denoted by the following equation.

  $Br_2(aq) + 2H_2O(l) \rightleftharpoons HBrO(aq) + H_3O^+(l) + Br^-(aq)$

In solution, $Br_2(aq)$ is brown, $Br^-(aq)$ is colourless and HBrO (hypobromic acid —a
weak acid) is colourless. When sodium hydroxide is added to the solution, the solution

* In CH_3I, radioactive isotope of iodine, ^{131}I is used

becomes colourless but the colour returns when hydrochloric acid is added. Explain this observation

9.8   The equilibrium constant for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
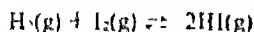
is 0.35 at 298K. In the following mixture at 298K, has equilibrium been reached? If not, state on which side of the equilibrium the system is

(i) p_{H_2} 0.10 atm and p_{H} 0.80 atm and there is solid I_2 in the container
(ii) p_{H_2} = 0.55 atm and p_{H} 0.44 atm, and there is solid I_2 in the container.
(iii) p_{H_2} 2.5 atm and p_{HI} 0.15 atm, and there is solid I_2 in the container

9.9   If 1 mole of H_2O and 1 mole of CO are taken in a 10 litre vessel and heated to 725K. At equilibrium 40 per cent of water (by mass) reacts with carbon monoxide according to the equation.

$$H_2O\,(g) + CO\,(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction

9.10 At 700 K the equilibrium constant for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI\,(g)$$

is 54.8. If 0.5 mole/litre of HI (g) is present at equilibrium at 700 K, what are the concentrations of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K

9.11 The equilibrium constant at 278 K for

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

is 2.0×10^{15}. In a solution in which copper has displaced some silver ions from solution, the concentration of Cu^{2+} ions is 1.8×10^{-2} mol L^{-1} and the concentration of Ag^+ ions is 3.0×10^{-9} mol L^{-1}. Is this system at equilibrium?

9.12 For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase·

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
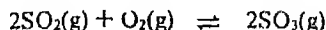
$K_p = 40.5$ atm^{-1} at 900 K and $\Delta H = -198$kJ

(i) Write the expression for the equilibrium constant for the reaction
(ii) At room temperature ($\simeq$ 300 K) will K_p be greater than, less than or equal to K_p at 900 K.
(iii) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant; what happens?
(iv) What is the effect of adding 1 mole of He(g) to a flask containing SO_2, O_2 and SO₃ at equilibrium at constant temperature

9.13 The dissociation of phosgene gas (COCl₂) is represented as follows:

$$COCl_2\,(g) \rightleftharpoons CO(g) + Cl_2(g)$$

When a mixture of these three gases at equilibrium is compressed at constant

temperature, what happens to (i) the amount of CO in the mixture (ii) the partial pressure of $COCl_2$ (iii) the equilibrium constant for the reaction

9 14 The ester, ethyl acetate, is formed by the reaction of ethanol and acetic acid and the equilibrium is represented as

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$
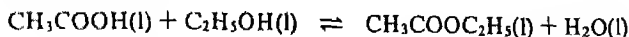
  (i) Write the concentration ratio, Q, for this reaction Note that water is not in excess and is not a solvent in this reaction.
  (ii) At 293 K, if one starts with 1.000 mol of acetic acid and 0.180 of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture Calculate the equilibrium constant.
  (iii) Starting with 0.500 mol of ethanol and 1 000 mol of acetic acid and maintaining it at 293K, 0 214 mol of ethyl acetate is found after some time Has equilibrium been reached?
  (iv) We do not use dilute aqueous solutions for this reaction Why?
  (v) Why is some concentrated sulphuric acid usually added to the reaction mixture in a laboratory preparation of ethyl acetate
  (vi) Since the heat of reaction is nearly zero for this reaction, how will the equilibrium constant depend upon the temperature?

9.15 Write the correctly balanced net ionic equation for the reaction whose equilibrium constant at 298K is.

  (a) $K_a(C_6H_5COOH) = 6.3 \times 10^{-5}$ (f) $K_a(H_2S) = 1 0 \times 10^{-7}$
  (b) $K_a(H_2C_2O_4) = 5 4 \times 10^{-2}$ (g) $K_a(HCN) = 4.0 \times 10^{-10}$
  (c) $K_a(HSO_3^-) = 2 8 \times 10^{-7}$ (h) $K_b(NH_3) = 1 8 \times 10^{-5}$
  (d) $K_b(OCl^-) = 9 1 \times 10^{-7}$ (i) $K_a(H_2S) = 1 0 \times 10^{-7}$
  (e) $K_b(CH_3NH_2) = 4.4 \times 10^{-5}$

9.16 (i) At 298K calculate the pH of (a) 0 200 M solution of methylamine, CH_3NH_2 (ionisation constant $= 4.4 \times 10^{-5}$).(b) 0.23 M weak acid HX (ionisation constant $= 7 3 \times 10^{-6}$)
  (ii) At 298K the pH of a solution of lemon juice is 2 32, What are the $[H_3O^+]$ and $[OH^-]$ in this solution?

9.17 (i) State the formula and name of the conjugate base of each of the following acids.
     (a) H_3O^+ (b) HSO_4^- (c) NH_4^+ (d) HF (e) CH_3COOH (f) $CH_3NH_3^+$
     (g) H_3PO_4 (h) $H_2PO_4^-$
  (ii) State the formula and name of the conjugate acid of each of the following bases·
     (a) OH^- (b) HPO_4^{2-} (c) $H_2PO_4^-$ (d) CH_3NH_2 (e) CO_3^{2-}
     (f) NH_3 (g) CH_3COO^- (h) HS^-
  (iii) Discuss the Lewis definition of acid and base How is it more useful than the Bronsted definition.

9.19 (i) What is the pH of an aqueous solution with hydrogen ion concentration equal to $3 \times 10^{-5} mol.L^{-1}$? What is the concentration of hydrogen ions in the solution? What is the pH of the solution? Is the solution acidic, basic or neutral?

9.20   Find the pH of the following solutions:
        (i)   3.2 g of hydrogen chloride dissolved in 1.00 L. of water
        (ii) 0.28 g of potassium hydroxide dissolved in 1.00 L. of water

9.21   The ionic product of water is 0.11×10^{14} at 273K; 1.0×10^{14} at 298 K and 51×10^{14} at 373 K. Deduce from this data whether the ionisation of water to hydrogen and hydroxide ions is exothermic or endothermic.

9.22   The solubility of CaF_2 in water at 298K is 1.7×10^{3} grams per 100 cm^3. Calculate the solubility product of CaF_2 at 298K.

9.23   If 25.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 25.0 cm^3 of 0.020 M NaF, will any BaF_2 precipitate? K_{sp} of BaF_2 is 1.7×10^{6} at 298 K.

U N I T 10

REDOX REACTIONS

Where there is oxidation, there is always reduction—chemistry is essentially a study of redox systems.

OBJECTIVES

In this Unit, we shall learn

* the meaning of 'oxidation' and 'reduction' as applied to chemical changes;

* to write the equation for an electrode reaction and describe an electrochemical cell.

* the dependence of EMF of a cell on concentration and temperature;

* the phenomenon of electrolysis;

* the determination of the oxidation number of an element in a compound;

* the use of the oxidation number for balancing a chemical equation.

YOU MUST HAVE COME ACROSS various types of reactions by this time. We know that oxygen reacts with carbon, sulphur and phosphorus and forms carbon dioxide, sulphur dioxide and phosphorus pentoxide respectively Similarly hydrogen reacts with oxygen and chlorine and forms water and hydrogen chloride. Such reactions fall in the category of a specific type of reactions called REDUCTION-OXIDATION or REDOX reactions. According to early views, oxidation was defined as the addition of oxygen or the removal of hydrogen Similarly reduction was defined as the addition of hydrogen or the removal of oxygen. No oxidation process can take place without a corresponding reduction These views can be suitably explained by the following examples·
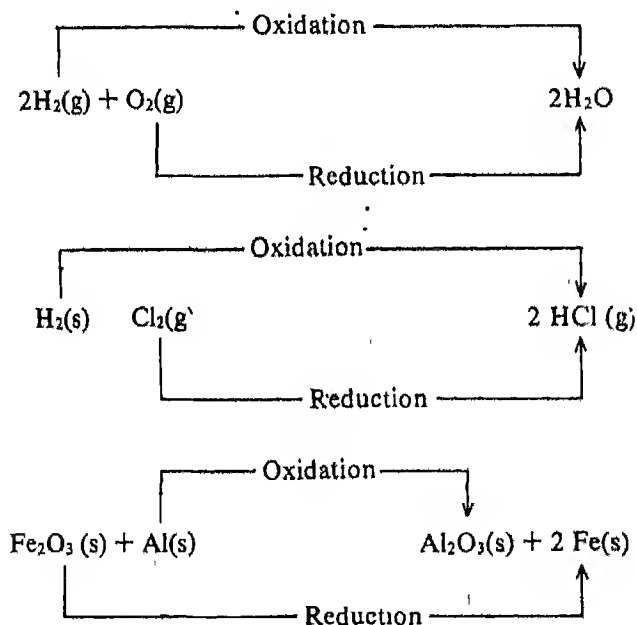
The substance that provides the oxygen or removes the hydrogen is called an OXIDISING AGENT. Oxygen, chlorine and iron oxide in the above reactions are called oxidising agents. These oxidising agents get reduced during the reaction. Similarly, a substance that provides the hydrogen or removes the oxygen is a REDUCING AGENT Hydrogen and aluminium in the above reactions are reducing agents. They are oxidised during the reaction.

10.1   OXIDATION AND REDUCTION AS AN ELECTRON TRANSFER PROCESS

If you burn a magnesium wire in oxygen, you will find a white powder. The reaction

can be written as

$$2 Mg(s) + O_2(g) \longrightarrow 2 MgO \ (s)$$
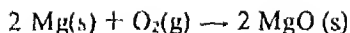
According to early definitions of oxidation and reduction, magnesium is oxidised as it has combined with oxygen. Now if you consider the formation of magnesium oxide based on the electronic configuration of magnesium and oxygen, you will find that during oxide formation magnesium is converted into its positive ion

$$Mg \longrightarrow Mg^{2+} + 2e^-$$
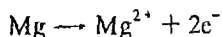
Where have these electrons gone? For answering this, you consider what happens to oxygen. Oxygen is converted to negatively charged oxide ion.

$$O + 2e^- \longrightarrow O^{2-}$$

Or

$$O_2(g) + 4e^- \longrightarrow 2O^{2-}$$

We can write

$$2 \overset{..}{M}g + (.\overset{.}{O}:)_2 \longrightarrow 2[Mg.\overset{.}{O}:] \longrightarrow 2 Mg^{2+}O^{2-}$$
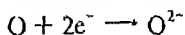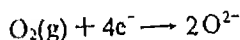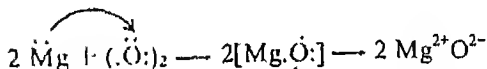
Similarly we can explain the reaction between magnesium and chlorine

$$\overset{..}{M}g + (:\overset{.}{C}l.)_2 \longrightarrow Mg^{2+} (.\overset{..}{\overset{.}{C}l}^-)_2$$
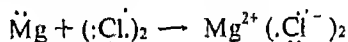
In the above two examples, electrons are donated by the magnesium atom to one oxygen atom or to two chlorine atoms. The effective number of electrons of the Mg atoms has decreased leading to a net positive charge near the magnesium and the effective number of electrons of the chlorine atom or oxygen atom has increased. Both the above reactions are oxidation-reduction reactions or REDOX REACTIONS. Now we can explain a redox reaction in terms of electron transfer. *A redox reaction is a reaction in which electrons are transferred from one reactant to another* Oxidation is loss of electrons or gain in positive valency. Similarly reduction is gain of electrons or loss of positive valency. The reactant which accepts electron (s) from the other reactant is reduced and is called the oxidising agent or oxidiser. The reactant which gives out electron (s) to the other reactant is oxidised and is called the reducing agent or reducer.

Let us consider the following experiment:

Strips of zinc and copper are cleaned with a sand paper and washed. The zinc strip is immersed in a solution of copper sulphate kept in a beaker 'A' and the copper strip is immersed in a solution of silver nitrate kept in beaker 'B' (Fig. 10.1) If we wait for five minutes and remove the strips of zinc and copper, we find changes over the surface of the strips. Why do these changes occur on the surface? This is due to a redox reaction taking place in these beakers. In aqueous solution, $CuSO_4$ dissociates into Cu^{2+} and SO_4^{2-} ions. When a zinc strip is dipped in copper sulphate,

reaction is as follows

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq) + SO_4^{2-}(aq)$$

Or $\qquad Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$

Oxidation and reduction can be depicted as

(2 electrons lost)
┌──────── Oxidation ────────┐
$Zn + Cu^{2+}(aq) \longrightarrow (Cu(s) + Zn^{2+}(aq)$
└──────── Reduction ────────┘
(2 electrons gained)
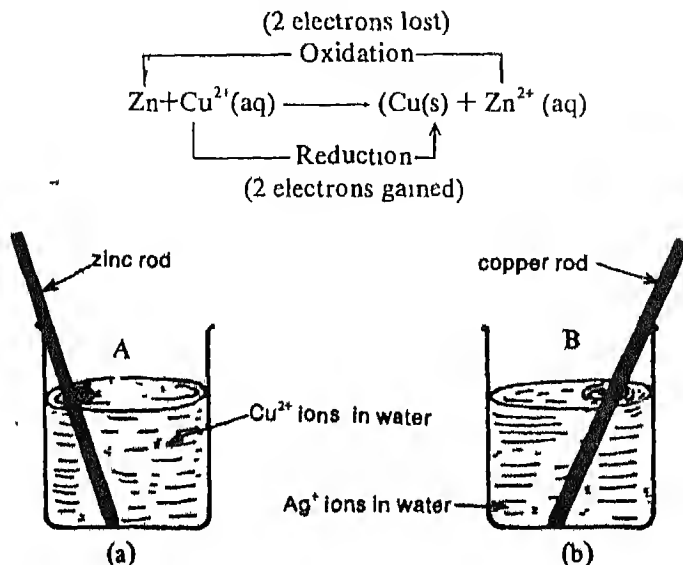
Fig. 10.1(a) *Zinc will dissolve and get converted to Zn^{2+} ions and Cu^{2+} ions will get reduced and would deposit on zinc metal (b) copper will dissolve to oxidise to Cu^{2+} ions, and Ag^+ ions will get reduced and deposited as silver on the copper rod*

This reaction is commonly described as Zn having displaced Cu^{2+} ions from the aqueous solution. Similarly the reaction between copper and $AgNO_3$ solution in beaker 'B' can be depicted as follows.

(2 electrons gained)
┌── Reduction ──┐
$Cu(s) + 2Ag^+(aq) \longrightarrow 2Ag + Cu^{2+}(aq)$
└──────── Oxidation ────────┘
(2 electrons lost)
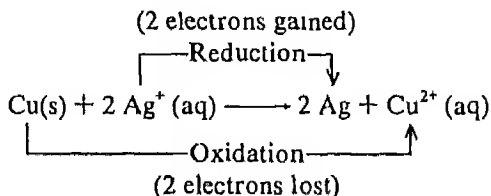
In the first reaction oxidation of zinc does not occur unless Cu^{2+} ion accepts electrons. Reduction of copper ion cannot occur unless electrons are obtained from zinc. Thus, oxidation and reduction are complementary processes and one cannot occur unless the other occurs simultaneously. One reactant is oxidised at the same time as the other reactant is reduced.

Let us consider the displacement of copper ions from the solution of copper sulphate by zinc. The reaction can be represented stepwise as follows:

$$Zn(s) \longrightarrow Zn^{2+} (aq) + 2e^- \qquad \text{(oxidation)}$$

$$Cu^{2+} (aq) + 2e^- \longrightarrow Cu (s) \qquad \text{(reduction)}$$
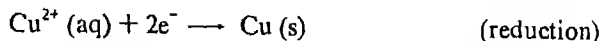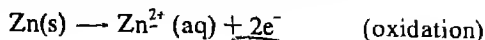
Most of the redox reactions can be written using two such half equations In the equation for the total reaction, the number of electrons lost must be equal to the number of electrons gained. This sometimes requires adjustment For example, in case of aluminium metal displacing silver from a solution of silver nitrate we get the following reactions.

$$Al(s) \longrightarrow Al^{3+} (aq) + 3e^- \qquad \text{(i)}$$

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{(ii)}$$
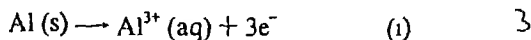
Before adding these two half equations, we must adjust (ii) by multiplying all items by three. By doing so the number of electrons involved in the reduction of silver ions equals the number of electrons lost by aluminium atom by oxidation We get the final equation:

$$Al(s) \longrightarrow Al^{3+} (aq) + 3e^-$$

$$3(Ag^+(aq) + e^- \longrightarrow Ag(s))$$

$$Al (s) + 3 Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3 Ag(s)$$
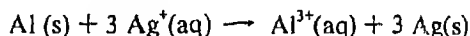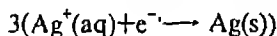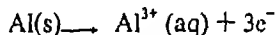
10 2 REDOX REACTIONS IN AQUEOUS SOLUTIONS-- ELECTROCHEMICAL CELLS

We have just seen that when a zinc strip is dipped in a beaker containing copper sulphate solution, copper is deposited over it. The reaction is written as follows:

$$Zn(s) \longrightarrow Zn^{2+} (aq) + 2e^-$$

$$Cu^{2+} (aq) + 2e^- \longrightarrow Cu (s)$$
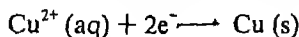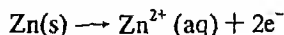
Overall reaction. $Zn (s) + Cu^{2+} (aq) \longrightarrow Zn^{2+} (aq) + Cu (s)$

Here, zinc metal is giving out electrons and is in direct contact with Cu^{2+} ions. We can make the same reaction take place even if the copper ions and zinc metal are not directly in contact. Let us perform the following experiment.

Zinc sulphate solution is taken in a beaker and a zinc strip is dipped in it. Similarly copper sulphate solution is taken in another beaker and a copper strip is dipped in it We now get two sets in two beakers and these are represented as: $Cu(s)/Cu^{2+}(aq)$ and $Zn(s)/Zn^{2+}(aq)$. Here, the line (/) represents an interface between two phases (e.g., solid/liquid or liquid/gas). Connect copper and zinc strips through an ammeter and resistance (5 Ohms) as shown in Fig. 10.2 Now cut a strip

of filter paper and soak it in a solution of potassium nitrate Put the soaked filter paper strip between two beakers so as to have contact between two solutions of copper sulphate and zinc sulphate What do you observe in the ammeter? A deflection in ammeter indicates a current. This current is due to the chemical reactions taking place in the two beakers.
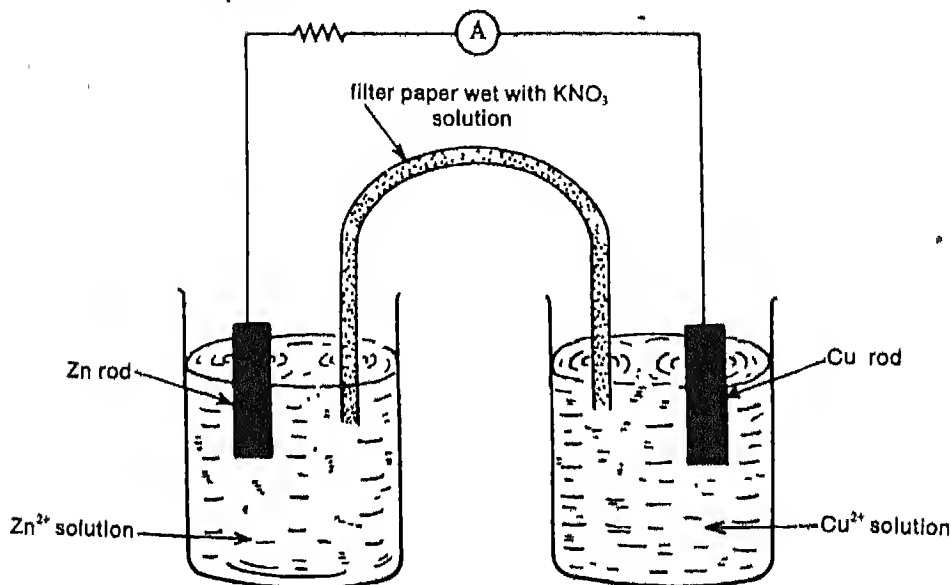
Fig. 10.2 *A galvanic cell*

During the reaction, zinc atoms go into solution as Zn^{2+} ions leaving electrons on the zinc strip. These released electrons flow through the external wire, resistance and ammeter and reach the copper strip At the copper strip, electrons react with Cu^{2+}, and the copper atoms formed will be deposited on the strip. The flow of charges is completed by the movement of ions in the two solutions. The sodium and nitrate ions present in the soaked filter paper, play a very important role of moving the charges between the two half cells. The two strips of copper and zinc dipped in their respective solutions are called electrodes and this set-up which generates electricity from a chemical reaction, is called a GALVANIC* CELL or ELECTROCHEMICAL CELL.

The electrode at which oxidation takes place is *anode* and the electrode at which reduction takes place is *cathode*. In this case the zinc electrode is *anode* because at this electrode, *oxidation* occurs:

$$Zn(s) \longrightarrow Zn^{2+} (aq) + 2e^-$$

---
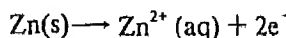
* L Galvani (1786) discovered this type of cell and therefore it goes through his name as 'galvanic cell'

and the copper electrode is *cathode* because at this electrode *reduction* occurs

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
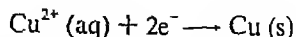
We can use different types of cathodes and anodes depending upon the electrolytic solutions we take. In this particular cell, the anode must be made of zinc (or else the cell would have a different reaction) but the cathode may be copper or platinum or carbon or some other metal that remains inert under these conditions. The deposited copper metal over any such electrode will work like a Cu/Cu^{2+} system. Note that the direction of the current is, by convention, opposite to the direction of flow of electrons. This arises because subsequent discoveries led to the knowledge that electrons carry a negative charge which again is just a convention since a positive direction had already been defined for the direction of flow of current.

10.3 EMF OF A GALVANIC CELL

In the cell shown in Fig. 10 2, a current flows through the circuit which is indicated by an ammeter. When a current flows between two points, a difference of potential is said to exist between them. *The potential difference is also given a special name* ELECTRO MOTIVE FORCE (EMF) This EMF is the result of redox processes occurring at the two electrodes of the cell. The EMF of a cell is, in fact, the contribution of the two half cells.

We have seen in Unit 9 that salts, acids and bases dissociate into ions in aqueous solutions. Such solutions conduct electricity because the ions (being charged) can transport charges across the solution from one electrode to another. What happens when a Cu strip is dipped in a solution containing Cu^{2+} ions. The Cu has a tendency to lose electrons and form Cu^{2+} ions which go into solution. However, in doing so, the copper strip develops a negative charge (because the negatively charged electrons released accumulate on the metal from the neutral state it started with) and hence would re-attract Cu^{2+} ions. Thus the Cu metal cannot keep on losing electrons and eventually an equilibrium would be reached which we can write as:

$$Cu(s) \rightleftharpoons Cu^{2+} + 2e^-$$
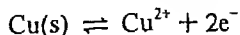
Therefore,
$$\frac{[Cu^{2+}(aq)][e^-]^2}{[Cu(s)]} = K$$

Or
$$[Cu^{2+}(aq)] = K[Cu(s)] = K,$$

since we put $[Cu(s)] = 1$ and $[e^-]^2 = 1$,

following conventions discussed in Unit 9

When such an equilibrium is reached, it
results in a separation of charges about
which you will learn in your physics
course This separation of charges leads
to a potential being developed between
the electrode and the solution From this,
we can see that the net charge separation
and hence the potential difference at
equilibrium depends on:

1. the metal and its ions
2. the concentration of the ions in the solution, and
3. temperature
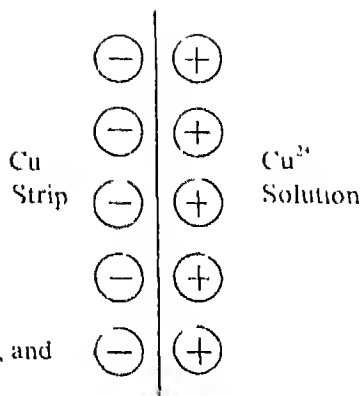
We also realise that if the Cu^{2+} ions are removed from near the electrode, more
Cu would get dissolved and vice versa. If the electrons are removed from the metal
there would be an increase in $[Cu^{2+}]$ ions near the electrode and this would be
counteracted by $[Cu^{2+}]$ from the solution getting deposited as Cu metal (Le
Chatelier's principle). The tendency for a metal to get oxidised or its ion to get
reduced to the metal is measured by the equilibrium constant K We can also
express it in terms of the potential developed between the metal in contact with a
solution of its ions. Since the potential developed depends on the concentration of
the ions, *we adopt a standard, namely, a 1 mol L^{-1} solution of ions, we thus define
a standard potential for a half-cell.*

$$Cu^{2+} (1 \text{ mol } L^{-1}, aq) + 2e^- \longrightarrow Cu(s)$$
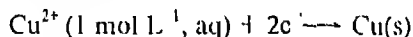
This is written as a reduction reaction and hence it used to be called standard
reduction potential. By convention, the half cell has been denoted as an electrode
and a *standard electrode potential* is defined as the standard potential for a half cell
described by a reduction reaction, as given above (Remember an electrode potential
refers to the combination of an electrode and ions and not just the electrode alone.)

A half cell by itself cannot cause movement of charges (flow of electricity) since,
once equilibrium is reached between the electrode and the solution, there is no
further net displacement of charges. It is also clear that different metal/metal ion
combinations would have different electrode potentials; hence we should combine two
half cells in such a manner that the electrons removed from one electrode (or half cell) is
fed into the other electrode (by an external conductor). Then it could so happen that
in the first electrode the equilibrium is shifted to the left.

$$M_1^+ + e^- \rightleftharpoons |M_1$$
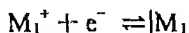
And in the second electrode the equilibrium is shifted to the right.

$$M_2^+ + e^- \rightleftharpoons M_2$$
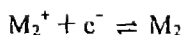
In so doing we can establish a situation where

$$M_2^+ + M_1 \longrightarrow M_2 + M_1^+$$
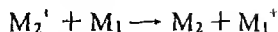
occurs because the free energy change in such a combination is less than 0

A single electrode potential itself can never be measured directly since as soon as another metal conductor is put into the solution it will set up its own potential *An electrode potential* therefore has to be measured against some *reference standard.* The standard reference electrode against which all other potentials are measured is the STANDARD HYDROGEN ELECTRODE (Fig. 10 3) The electrode potential of this electrode is assigned a value of zero
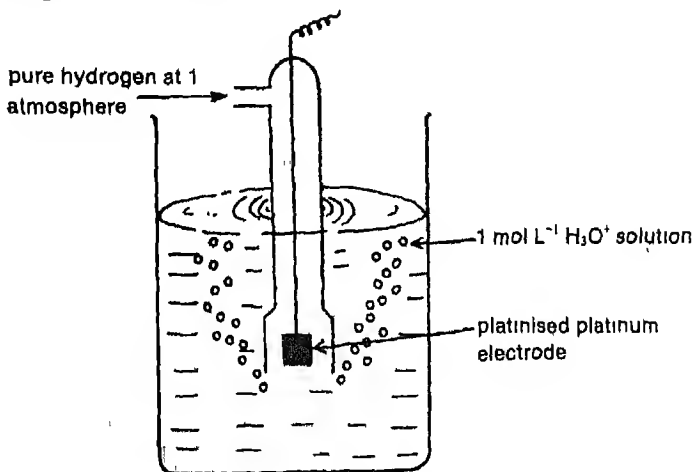
Fig. 10.3 *Standard hydrogen electrode*

In a standard hydrogen electrode, a platinised platinum electrode is dipped in 1 mol L^{-1} solution of hydrogen ion (H$^+$), to be exact (H$_3$O$^+$) at 298 K and pure hydrogen gas, maintained at one atmospheric pressure, is bubbled over the platinised platinum electrode. Platinised platinum acts as a catalyst to increase the speed of attainment of equilibrium between H$_2$ and H$_3$O$^+$

For measuring a standard electrode potential a half cell, that is, the electrode formed by metal/metal ions (with a metal ion concentration of 1 mol L^{-1}) is connected to a standard hydrogen electrode via a salt bridge (Fig. 10.4). A salt bridge is to provide a low resistance electrical connection between the two half-cells, without any additional difference in potential being developed at the various other junctions, such as solution in half-cell (1)/salt bridge/half cell (2) At the same time the two half cells are physically separated For preparing a salt bridge agar-agar is
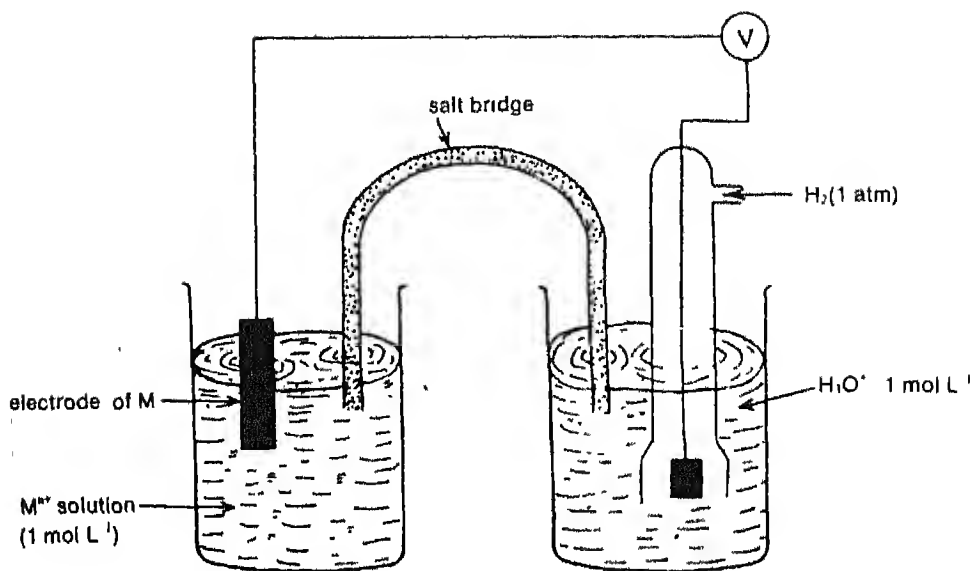
Fig. 10.4 *Measurement of standard electrode potential*

dissolved in a hot aqueous solution of KNO_3 or KCl and filled in a U-shaped glass tube. On cooling, the agar-agar solution becomes solid and can be used conveniently as a salt bridge The potential difference developed is measured using a potentiometer or high resistance voltmeter   Since the hydrogen electrode is arbitrarily assigned a potential of zero, the entire cell EMF is ascribed to the connected electrode In this assembly if the measured voltage is such that *the connected electrode forms the negative side of the cell, it will be allotted a negative electrode potential and if it forms the positive side, it will be allotted a positive electrode potential The standard electrode potential for $Cu(s)/Cu^{2+}(aq)$ (1 mol L* $^{-1}$*) is $+ 0 34$ V and for $Zn/Zn^{2+}(aq)$ (1 mol L* $^{-1}$*) is $- 0.76$ V This means that the standard Zn/Zn^{2+} electrode will be the negative side and the standard Cu/Cu^{2+} electrode will be the positive side when connected respectively to a hydrogen electrode* (Fig. 10.5)

The values of some standard electrode potentials at 298K are given in Table 10.1. (The electrode potentials are often called STANDARD REDOX POTENTIALS). In Table 10.1 the elements are arranged in a series. This arrangement of elements in a series is sometime called ACTIVITY SERIES. By using this series, we can compare the reducing and oxidising capability of a particular element. A metal higher up in this series is a better reducing agent in aqueous solution than one that lies below it. Thus zinc can displace tin, lead, copper and others below it from aqueous solutions of their salts. However, under the same conditions tin cannot displace Zn from a Zn^{2+} solution.
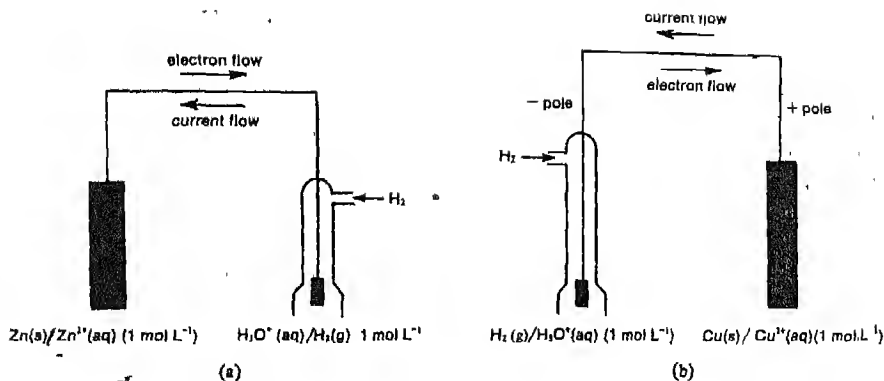
Fig. 10 5   *Determining standard electrode potenti* '   - - '- ' ' '.   '   ' **(a)** *Zn (s)/Zn²⁺*
(aq) forms negative side of the cell and therefore   ·   ·   .   '*d* **(b)** *Cu(s)/Cu²⁺*
(aq) forms positive side of the cell and therefore is given positive electrode potential

We have just seen that a metal in contact with its ions forms a half cell and
when we join two half cells together with the help of a salt bridge, we get an
electrochemical cell For example, Daniel cell is made of two half cells· Zn (s) /
Zn^{2+} (aq) and Cu/Cu^{2+}(aq) In depicting a cell, by convention, the half cell in which
oxidation takes place is written on the left hand side and the electrode becomes the
anode, and the other half cell in which reduction occurs is written on the right hand
side and the electrode becomes the cathode Whether a particular electrode will
work as cathode or anode in a combination, will be decided on the basis of its
electrode potential. Daniel cell is represented as

$$Zn(s)/Zn^{2+}(aq) \quad || \quad Cu^{2+}(aq)/Cu(s)$$
$$- (\text{Anode}) \qquad + (\text{Cathode})$$
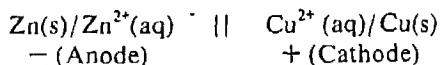
- indicates interface between two different phases such as solid/solution or
   gas/solution
   indicates a physical separation but with electrical conductivity such as a
   porous pot, salt bridge, etc

TABLE 10 1

Standard Electrode Potentials at 298 K

Elements	Electrode Reaction	E_{298}^{0} (Volts)
Li	$Li^+(aq)+e^- \rightarrow Li(s)$	-3.05
K	$K^+(aq) + e^- \rightarrow K(s)$	$-2\,93$
Ba	$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	$-2\,90$

Elements	Electrode Reaction	E°_{298} (Volts)
Ca	$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	$- 2.87$
Na	$Na^+(aq) + e^- \rightarrow Na(s)$	$- 2.71$
Mg	$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	$- 2.37$
Al	$Al^{3+}(aq) + 3e \rightarrow Al(s)$	$- 1.66$
H_2	$2H_2O + 2e \rightarrow H_2(g) + 2OH^-(aq)$	$- 0.83$
Zn	$Zn^{2+} + 2e \rightarrow Zn(s)$	$- 0.76$
Cr	$Cr^{3+}(aq) + 3e \rightarrow Cr(s)$	$- 0.74$
Fe	$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	0.44
Cd	$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$	$- 0.40$
Pb	$PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(aq)$	$- 0.31$
Co	$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	$- 0.28$
Ni	$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	$- 0.25$
Sn	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$- 0.14$
Pb	$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	0.13
H_2	$2H^+(aq) + 2e \rightarrow H_2(g)$ (standard electrode)	0.00
Cu	$Cu^{2+}(aq) 2e \rightarrow Cu(s)$	$+ 0.34$
I_2	$I_2(s) + 2e \rightarrow 2I^-(aq)$	$+ 0.54$
Fe	$Fe^{3+} + e \rightarrow Fe^{2+}(aq)$	$+ 0.77$
Hg	$Hg_2^{2+}(aq) + 2e \rightarrow 2Hg(l)$	$+ 0.79$
Ag	$Ag^+(aq) + e \rightarrow Ag(s)$	$+ 0.80$
Hg	$Hg^{2+}(aq) + 2e \rightarrow Hg(l)$	$+ 0.85$
Br_2	$Br_2(aq) + 2e \rightarrow 2Br^-(aq)$	$+ 1.08$
O_2	$\tfrac{1}{2}O_2(g) + 2H_3O^+(aq) + 2e \rightarrow 3H_2O$	$+ 1.23$
Cl_2	$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$	$+ 1.36$
Au	$Au^{3+}(aq) + 3e \rightarrow Au(s)$	$+ 1.42$
Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e$	
	$\rightarrow Mn^{2+}(aq) + 12H_2O(l)$	$+ 1.51$
F_2	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	$+ 2.87$

The EMF of the cell in the standard state, E°, is expressed as

$$E^\circ = E^\circ_{right} - E^\circ_{left}$$

The cell reaction of a Daniel cell is·

~~Right~~ :   Oxidation $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

~~Left~~ ·   Reduction $\underline{Cu^{2+}(aq) + 2e \rightarrow Cu(s)}$

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$
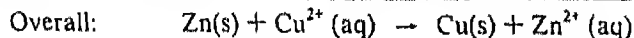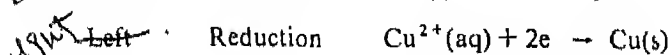
Here E°_{right} and E°_{left} are standard electrode potentials of the right and left electrodes (or half cells) respectively. (The superscript o denotes standard state). In the Daniel cell, standard electrode potential of $Zn(s)/Zn^{2+}(aq)$ (1 mol L^{-1}) is $- 0.76$ V and that of $Cu(s)/Cu^{2+}(aq)$ (1 mol L^{-1}) is $+ 0.34$ V, then

$Cu/Cu^{2+} \quad Zn/Zn^{2+}$
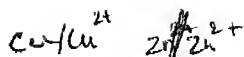
$$E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left} = 0.34V - (-0.76V) = 1 \ 10V$$

If you see Table 10.1 carefully, you will find that standard electrode potentials correspond to reduction reactions. This is why earlier they used to be mentioned as STANDARD REDUCTION ELECTRODE POTENTIAL For the reactions which are written in the opposite way, i.e , as an oxidation reaction, the electrode potential was referred to as STANDARD OXIDATION ELECTRODE POTENTIAL. This potential will have the same magnitude but opposite sign as compared to the reduction electrode potential For example, if the reduction potential of the electrode, Zn/Zn^{2+} (aq) for the reaction, $Zn^{2+} + 2e^{-} \longrightarrow Zn(S)$ is -0.76 V, then its oxidation potential for the oxidation reaction, $Zn(s) \longrightarrow Zn^{2+}$ (aq) $+ 2e^{-}$ will be $+ 0.76$ V Tabulation of electrode potentials as standard reduction potentials and standard oxidation potenials is no more in practice. According to the International Union of Pure and Applied Chemistry (IUPAC), the term 'standard potential' should be used for the reactions written as reduction reactions.

We can take various combination of half cells and construct a number of electrochemical cells The EMF of such cells in standard state can be calculated using the equation,

$$E^{\circ} = E^{\circ}_{right} - E^{\circ}_{left}$$

Similar to metals, the standard electrode potential for non-metals that produce negative ions in aqueous solution can be determined The standard electrode potential of chlorine can be determined by using an electrode consisting of chlorine gas at one atmospheric pressure in equilibrium with 1M solution of chlorine ion, $Cl_2(g) + 2e^{-} \longrightarrow 2Cl^{-}$ (aq). The standard electrode potential of bromine, iodine, etc. are also given in Table 10.1 along with the standard electrode potentials of metal/metal ions.

For metals of variable valency, the redox potential for one ion in equilibrium with another of different charge can be determined. For example, iron exists in two forms.

$$Fe^{2+} \text{ and } Fe^{3+}$$

The redox potential of the system, $Fe^{2+}(aq)/Fe^{3+}$ (aq) is obtained by measuring the EMF of the cell given below with Pt wire being the inert electrode.

$$\text{Pt, } H_2(g)/H_3O^{+} \text{ (aq)} \ || \ Fe^{3+}(aq); Fe^{2+}(aq)/Pt$$
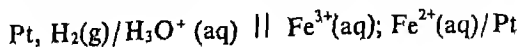
10.4 DEPENDENCE OF EMF ON CONCENTRATION AND TEMPERATURE

The way in which the electrode potential of a metal is related to the metal ion concentration and the temperature is given by the Nernst equation

$$E = E^o + \frac{RT}{nF} \ln [M^{n+} (aq)]$$

Here E is the electrode potential, E^o is the standard electrode potential (for a molar solution of a metal ion, M^{n+} at 298K), R is the gas constant and is approximately 8.31 $JK^{-1}mol^{-1}$, T is the temperature in Kelvin, n is valency of the metal, F is Faraday (=96,500 Coulomb), ln represents natural logarithm (to the base e). The above equation can be verified by measuring the electrode potential at different concentrations of the metal ion by connecting the metal/metal ion half cell via a salt bridge to a standard hydrogen electrode. Let us consider the Daniel cell once again,

$$Zn(s)/Zn^{2+} (aq) \quad || \quad Cu^{2+} (aq)/Cu(s)$$

The electrode potential of the right half cell,

$$E_{right} = E^o_{right} + \frac{RT}{2F} \ln [Cu^{2+} (aq)]$$

Now cell potential E can be written as

$$E = E_{right} - E_{left} = E^o_{right} + \frac{RT}{2F} \ln [Cu^{2+}(aq)] - \left\{ E^o_{left} + \frac{RT}{2F} \ln [Zn^{2+}(aq)] \right\}$$

$$= (E^o_{right} - E^o_{left}) + \frac{RT}{2F} \ln \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]}$$

After substituting the value of the standard electrode potentials and converting natural logarithm to the base 10.

$$E(in\ Volts) = 1.1 + \frac{2.303RT}{2F} \log \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]}$$

$$= 1.1 + \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]}$$

at 298 K (with values substituted for R, T, F).

Suppose we take the concentration of copper sulphate solution as 0.01 M and that of zinc sulphate as 0.1 M at a temperature of 298 K. The EMF of the cell can be calculated by substituting the value of R, T, n, F and concentrations of Cu^{2+} and Zn^{2+} ions in the above equation

Here, $\qquad [Cu^{2+}(aq)] = 0.01$ M and $[Zn^{2+} (aq)] = 0.1$ M

Therefore, $\qquad E = 1.1 + \frac{0.059}{2} \log \frac{0.01}{0.1}$

$$= 1.1 + 0.0295 \log \frac{1}{10}$$

$$= 1.1 - 0\ 0295 = 1\ 07\ V$$

In the Daniel cell the valence of the zinc and copper is the same, i e., 2. Now let us take Ni/Ni^{2+} (aq) || Ag$^+$ (aq)/Ag cell in which the valences of the metals used in the two half cells are different.

$$Ni(s)/Ni^{2+}(aq)\ ||\ Ag^+\ (aq)/2\ Ag(s)$$

Cell reaction can be written as

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2\ Ag(s)$$
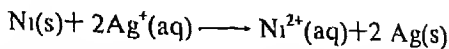
The electrode potential of silver and nickel half cells are given by

$$E_{Ag} = E^\circ_{Ag} + \frac{RT}{F} \ln [Ag^+(aq)], n = 1$$

or

$$E_{Ag} = E^\circ_{Ag} + \frac{RT}{2F} \ln [Ag^+(aq)]^2$$

and

$$E_{Ni} = E^\circ_{Ni} + \frac{RT}{2F} \ln [Ni^{2+}(aq)], n = 2$$

(In writing electrode potential of Ag/Ag$^+$(aq), we have to be careful in substituting the value of concentrations and valence During the reaction, two electrons are released from one Ni atom and therefore reduction of silver ion, i.e , Ag$^+$ + e$^-$ → Ag, should be multiplied by 2 to balance the electrons. *But remember, by multiplying by 2, the value E$^\circ$$_{Ag}$ remains unchanged.*

If the cell is allowed to function, silver is deposited and Ni^{2+} ions are formed. The EMF of the cell under these conditions is written as

$$E \text{ (in volts)} = E_{right} - E_{left}$$

$$= E^\circ_{Ag} + \frac{RT}{2F} \ln [Ag^+(aq)]^2 - \{E^\circ_{Ni} + \frac{RT}{2F} \ln [Ni^{2+}(aq)]\}$$

$$= (E^\circ_{Ag} - E^\circ_{Ni}) + \frac{RT}{2F} \ln \frac{[Ag^+(aq)]^2}{[Ni^{2+}(aq)]}$$

$$= 1.05 + 2.303 \frac{RT}{2F} \log \frac{[Ag^+(aq)]^2}{[Ni^{2+}(aq)]}$$

{Here, E$^\circ_{Ag}$ − E$^\circ_{Ni}$ is equal to [0.80 − (− 0 25)] = 1.05V}

Thus, the expression for EMF for a cell can be worked out depending upon the reactions occurring in the two half cells and the concentrations of the reactants.

10.5 ELECTROLYSIS

In the electrochemical cells we have an example in which chemical energy is converted into electrical energy. In fact there is a relationship between the change in free energy of the cell reaction and the EMF of the cell.
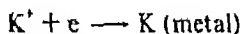
For a Daniel cell:

$$Cu^{2+}(c_1, aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(c_2, aq)$$

$$E = E^\circ + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Delta G = - nEF$$

and
$$\Delta G^\circ = - nE^\circ F$$

This is not surprising since we had in Unit 8 described the change in free energy as the maximum available work and one of the best ways to tap all the available chemical energy is to set up an electrochemical cell and discharge it, drawing extremely small currents.

In reverse, the passage of electricity through electrolytes may cause chemical changes, under some conditions. For example, Humphrey Davy (1807) isolated the element potassium by passing an electric current though molten potassium hydroxide. In solid potassium hydroxide, even though K^+ and OH ions exist they are not free to move. When the salt is molten, the ions K^+ and OH are free to move and they conduct the electriojty. The positive ions move towards the cathode where reduction (addition of electrons) can take place

$$K^+ + e \longrightarrow K \text{ (metal)}$$

and the negative ions move towards the anode, where oxidation takes place

$$2OH^- \longrightarrow H_2O + \tfrac{1}{2}O_2 + 2e^-$$

The passage of electricity through electrolytes leading to chemical changes is known as ELECTROLYSIS and the cell in which electrolysis occurs is known as an ELECTRO-LYTIC CELL *Many other metals such as Na, Ba, Sr, Ca and Mg can be isolated in a similar manner.*

To understand the phenomena of electrolysis, let us take solid lead bromide in a silica crucible and insert two graphite electrodes (these may be obtained from used torch cells). A D.C. voltage source, say two torch cells connected in series are connected through an ammeter to the electrode (Fig. 10.6). No current is observed. The crucible is heated and when the solid is molten a current passes and a red brown gas (bromine) evolves at the anode and metallic lead deposits at the cathode. The following reactions occur at the electrodes during the electrolysis:

At the cathode ,   (reduction) : $Pb^{2+}(l) + 2e^- \longrightarrow Pb(l)$

At the anode   :   (oxidation) : $2\ Br^-(l) \longrightarrow Br_2(g) + 2e^-$

at anode = oxidation = $2\ Br^- \rightarrow Br_2 + 2e^-$
       (+)
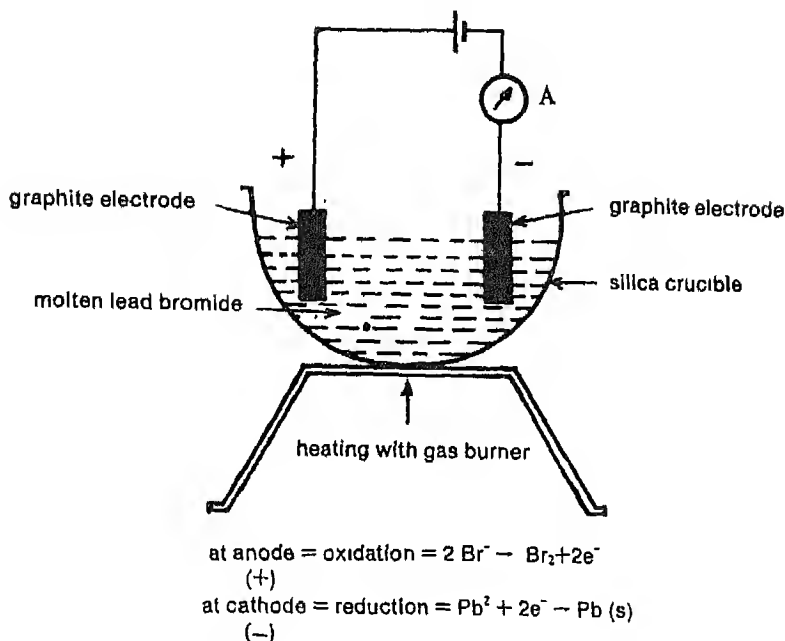at cathode = reduction = $Pb^2 + 2e^- \rightarrow Pb\ (s)$
       (–)

Fig. 10.6 *Electrolysing molten lead bromide*

Since *positively charged ions* move to the cathode in an electrolytic cell they are known as CATIONS *Negatively charged ions* move to anodes and are called ANIONS A few cations and anions are given below

$$Cations = Pb^{2+},\ Na^+,\ Li^+,\ Ca^{2+},\ Al^{3+}$$
$$Anions = SO_4^{2-},\ OH^-,\ Br^-,\ I^-,\ Cl^-$$

If a beaker of water with two graphite electrodes are connected to two torch cells in series (an arrangement similar to that shown in Fig 10 6), the ammeter will not show a measurable current. This is because water is a poor conductor of electricity. Addition of a few drops of dilute sulphuric acid makes the solution conduct electricity and at the anode, oxygen is produced and at the cathode, hydrogen is produced (Fig. 10.7). The volume of oxygen produced, if measured carefully, is found to be half that of the hydrogen. In fact this observation enabled early scientists to confirm that the molecular formula of water is H_2O. It is sufficient to say here that the reactions at the two electrodes are:

Cathode :   (Reduction) $2H^+(aq) + 2e \longrightarrow H_2(g)$

Anode   :   (Oxidation) $2OH^-(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g) + 2e$

Why OH^- is oxidised and not SO_4^{2-} which is present in the acidified water can be understood by consulting the standard redox potential table but we will postpone this discussion to the next year.

The extent of a chemical reaction will depend on the amount of electric charge transported through the cell (this will be proportional to the current and the time for which it was passed) and the chemical reaction (whether the redox reaction involves one or more electrons). Michael Faraday (1833) enunciated his famous laws of electrolysis that relate the extent of chemical change to the current, time of passage and the chemical reaction and we shall discuss them in the higher classes.

Electrolysis plays an important role in industry. Besides production of hydrogen, it is used in the production of sodium, potassium, magnesium, pure copper, aluminium and non-metals such as chlorine. It is also used in the production of heavy water (D_2O). Many organic redox reactions are carried out by electrolysis.

10.6 OXIDATION NUMBER

The concept of oxidation and re-
duction in terms of electron trans-
fer which we discussed in section
10.1, can be applied conveniently
to ionic reaction. However, we
cannot easily explain redox chan-
ges in terms of electron transfer
where covalent compounds are
involved. For convenience, che-
mists have adopted an arbitrary
system for treating oxidation-reduc-
tion phenomena in either covalent
or ionic substances This system
requires introduction of a term
OXIDATION NUMBER (or OXIDA-
TION STATE'). The change in oxida-
tion number of an element, in-
dicates that oxidation or reduction
has occurred. The *oxidation num-
ber is a charge assigned to an atom
of a compound or of an ion accord-
ing to some arbitrary rules.* (This

Fig. 10.7 *An apparatus for electrolysing acidified water*

number is fictitious in case of covalent species This number is roughly equivalent to the number of electrons, in the valence shell of an atom, that are gained or lost completely or to a large extent by that atom while forming a bond in a compound)
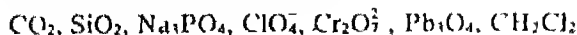
Rules for Assigning Oxidation Number: There is a set of rules to assign oxidation number to any atom, molecule or ion The rules are as follows:

1. The oxidation number of an element in its elemental form is 0 For example, H_2, P_4, S_8, O_2, Fe, Br_2 and Ag have oxidation number zero

2. The oxidation number of an element in a single (monatomic) ion is the charge on the ion For example, K^+ has an oxidation number $+1$, Ca^{2+} : $+2$, Al^{3+} $+3$, and Cl^- : -1

3. The oxidation number of elements in compounds or in compound ions is calculated in the following manner

   (i) Hydrogen is assigned oxidation number $+1$ and oxygen is assigned oxidation number -2 in almost all their compounds The exceptions occur when hydrogen forms compounds with active metals called 'metal hydrides, e.g., KH, MgH_2, CaH_2 and LiH. In these compounds, hydrogen has an oxidation number of -1 Similarly exceptions occur in case of oxygen when it forms peroxide and fluoride In case of Na_2O_2 (sodium peroxide) and H_2O_2, the oxidation number of oxygen is -1. In case of OF_2, oxygen has an oxidation number of $+2$.

   (ii) Fluorine is the most electronegative element and is assigned an oxidation number of -1 in all its compounds. For other halogens the oxidation number is always -1 except when they are bonded to a more electronegative halogen or oxygen For example, in IF_7 the oxidation number iodine is $+7$.

   (iii) The oxidation number of the alkali metals is $+1$ in all their compounds and the oxidation number of the alkaline earth metals is $+2$ in all their compounds.

   (iv) The algebraic sum of the oxidation number of all atoms in a neutral molecule is zero. If the substance is an ion rather than a molecule, the algebraic sum of the oxidation number of the atoms in the ion must equal the charge on the ion.

By applying these rules we can calculate the oxidation number of any element in a molecule or ion. For example, in H_2S there are two hydrogen atoms and each has an oxidation number $+1$; therefore the oxidation number of sulphur is -2. In sulphate ion, SO_4^{2-}, each oxygen has an oxidation number of -2. So counting all the oxygens, we get $4 \times (-2) = -8$. The oxidation number of sulphur must be $+6$ in order that the algebraic sum of the five atoms in SO_4^{2-} be equal to $(+6-8) = -2$, the charge on the ion.

Example 10.1

Taking the help of the rules given on page 299 calculate the oxidation number of all the atoms in the following compounds and ions.
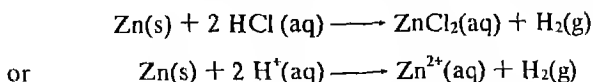
$$CO_2, SiO_2, Na_3PO_4, ClO_4^-, Cr_2O_7^{2-}, Pb_3O_4, CH_2Cl_2$$

Solution

		Oxidation number	Oxidation number of atoms
CO_2	Each oxygen −2 Total oxygen = −4	total charge (= 0) − (total oxygen = −4)	O 2
		Carbon = +4	C +4
SiO_2	Each oxygen −2 Total oxygen = −4	total charge (= 0) − (total oxygen = −4)	O 2
		Silicon = +4	Si +4
Na_3PO_4	each sodium +1 total sodium +3 each oxygen −2 Total sodium + oxygen = −5	total charge (= 0) − (total sodium + oxygen = −5)	Na +1 O −2
		Phosphorus = +5	P +5
ClO_4^-	each oxygen −2 Total oxygen = −8	total charge (= −1) − (total oxygen = −8)	O 2
		Chlorine = +7	Cl +7
$Cr_2O_7^{2-}$	each oxygen −2 Total oxygen = −14	total charge (= −2) − (total oxygen = −14)	O 2
		total chromium = +12 each chromium = +6	Cr +6
Pb_3O_4	each oxygen −2 total oxygen = −8	total charge (= 0) − (total oxygen = −8)	O −2
		Total lead = +8 each lead = $+\frac{8}{3}$	Pb $\frac{8}{3}$
CH_2Cl_2	each hydrogen +1 total hydrogen +2 each chlorine −1 total chlorine −2 total hydrogen + chlorine = 0	Total charge (= 0) − (total hydrogen + chlorine = 0)	H +1 Cl −1
		Carbon = 0	C 0

10 6 1 Redox Reactions in terms of Oxidation Number

A reaction will be considered as a redox reaction if there is a change in the oxidation number Let us consider the reaction between zinc and hydrochloric acid.
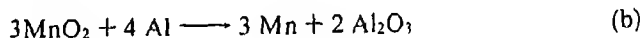
$$Zn(s) + 2\ HCl\ (aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

or $$Zn(s) + 2\ H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

In this reaction zinc is converted into Zn^{2+} (aq) by giving out two electrons and is oxidised. H^+ ion accepts electron and therefore is reduced Zinc is the reducing agent and H^+ is the oxidising agent Now let us consider this reaction taking the help of oxidation numbers.

We find that the oxidation number of zinc increases from 0 to +2 and it is oxidised. Also, the oxidation number of H^+ decreases from (+ 1) to 0 and it is reduced. Thus we conclude that *oxidation is an increase in oxidation number and reduction is a decrease in oxidation number* For further illustrating this, let us take a few more examples and calculate the oxidation number of the concerned element to decide oxidation and reduction.

$$2\ HI(aq) + Cl_2\ (aq) \longrightarrow I_2(s) + 2\ HCl(aq) \tag{a}$$

Change in oxidation numbers: I $= -1$ to 0, Cl: 0 to -1: H $+1$ to $+1$ (no change)

$$3MnO_2 + 4\ Al \longrightarrow 3\ Mn + 2\ Al_2O_3 \tag{b}$$

Change in oxidation numbers· Mn $+4$ to 0, Al $= 0$ to 3, O -2 to -2

$$2MnO_4^- + 10\ Cl^- + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 5\ Cl_2 + 8\ H_2O \tag{c}$$

Change in oxidation numbers. Mn· $+7$ to 2, O -2 to -2, Cl· -1 to 0
On the basis of the oxidation number we find that in equation:
(a) Iodine in HI is oxidised and chlorine is reduced
(b) Manganese in MnO_2 is reduced and aluminium is oxidised,
(c) Manganese in MnO_4^- is reduced and Cl^- is oxidised.

10.6.2 Oxidation Number and Nomenclature

The Roman numerals, used in the naming of compounds of metals are, in fact, the oxidation numbers of these elements. This system of naming is known as the Stock notation after the chemist who devised it For example, in two oxides of copper, Cu_2O and CuO, the oxidation numbers of copper are 1 and 2 respectively These compounds are known as Copper (I) and Copper (II) oxide respectively This notation is used for those metals which show more than one oxidation state or oxidation number Many more examples can be taken for illustration· Mn_2O_7 is written as Manganese (VII) oxide; V_2O_5 as Vanadium (V) oxide, $K_2Cr_2O_7$ as

potassium dichromate (VI); Cr_2O_3 as chromium (III) oxide, Na_2CrO_4 as sodium chromate (VI), $Fe_2(SO_4)_3$ as iron (III) sulphate; $FeSO_4$ as iron (II) sulphate, etc

Stock notation is not generally used for non-metals. Compounds such as PCl_3 and PCl_5 are distinguished by names phosphorus trichloride and phosphorus pentachloride respectively

10.7 BALANCING OF OXIDATION REDUCTION EQUATIONS

You must have seen that balancing of redox equation in electrochemical cells is easy and can be done by simple inspection. Such reactions actually occur in two steps and we denote them by *two half cells* Oxidation occurs in one half cell and reduction occurs in the other half cell. We take the help of half equations in balancing non-electrochemical reactions as well, irrespective of whether the total reaction occurs in two steps or not. *For balancing such redox reactions:*

   we first write the balanced half equation,

   then the half equations are combined to produce a balanced reaction equation

For balancing a redox reaction, there are some general rules which should be followed

(i) The molecular formula of the oxidising and reducing agents and the formula of the reduced and oxidised products should be known.

(ii) The law of conservation of mass should not be violated, i.e., the number of atoms of each element on one side of the equation must be equal to the number of atoms of the corresponding elements on the other side

(iii) Conservation of charge should not be violated. All the electrons produced in the oxidation half reaction must be used up by the reduction half reaction

Oxidation-reduction reactions occur in acidic, basic or neutral solutions. The method of balancing redox reactions for acidic and basic solutions are slightly different. If H^+, or any acid, appears on either side of the equation, the reaction takes place in acidic solution. If OH^-, or any base, appears on either side of the equation, the solution is basic. If neither H^+, OH^- nor any acid or base is present, the solution is neutral

For illustrating the method of balancing a redox reaction, let us take the reaction between iron (II) ions and dichromate ions in acidified solution and balance the equations resulting from the equation:
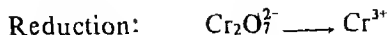
$$Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O$$

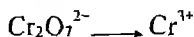Let us proceed stepwise:

Step 1. Find the elements whose oxidation numbers are changed:

$Cr_2O_7^{2-}$ (oxidation number of $Cr = +6$) is converted into Cr^{3+} (oxidation number of $Cr = +3$). Also Fe^{2+} (oxidation number of $Fe = +2$) to Fe^{3+} (oxidation number of

Fe = +3). Thus

$$\text{Oxidation} \qquad Fe^{2+} \longrightarrow Fe^{3+}$$

$$\text{Reduction:} \qquad Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Step 2· Balance each half equation separately·
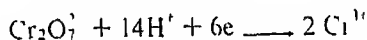Let us first take the reduction half equation for balancing

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

(a) *Balance half equation for all atoms other than H and O·* There are two chromium atoms on the left, one on the right Therefore
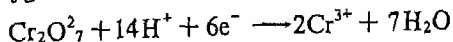
$$Cr_2O_7^{2-} \longrightarrow 2\, Cr^{3+}$$

(b) *Calculate the oxidation number on the left and on the right. Add electrons to Whichever side is necessary to make up for the difference:* The oxidation number of chromium on the left is +6 and on the right is +3 Each chromium atom must gain three electrons. Since there are two chromium atoms, six electons will be needed

$$Cr_2O_7^{2-} + 6e \longrightarrow 2\, Cr^{3+}$$

(c) *Balance the half equation so that both sides will have the same charge* Since reaction is taking place in an acidic medium, H^+ ion will be added to account for the extra positive charge on one side or the other The total charge on the left is −8, on the right + 6. Therefore, 14H⁺ ion will be needed to balance the charge,

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2\, Cr^{3+}$$

(d) *Add water molecules.to complete the balancing of the equation.* Since there are 14 hydrogen atoms and 7 oxygen atoms on the left side, $7H_2O$ is required on the right

$$Cr_2O^2_7 + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Now it becomes a balanced half equation Check again for the number of atoms and charge
    Let us now apply the same steps to balance the oxidation half equation.

$$Fe^{2+} \longrightarrow Fe^{3+}$$

(a) *Balance all the atoms other than H and O· It is not needed as it is already balanced.*
(b) *Add electrons to whichever side is necessary to make up for the difference in oxidation number.*

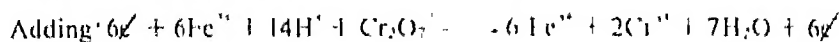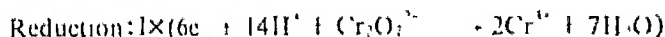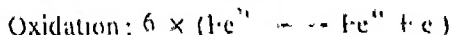   Oxidation number of Fe is +2 on the left side and +3 on the right, therefore one electron is needed
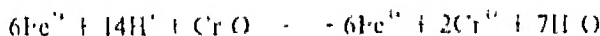
$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

(c) *Balance the charges* This is already done (both sides have a total charge of + 2).

(d) *Add water* In view of oxygen and hydrogen being absent, this step is not necessary.

Step 3. *Add two balanced half equations together Before doing this, ensure that electrons produced in oxidation are equal to the electrons used in reduction. If necessary, multiply the half equation by suitable numbers.*
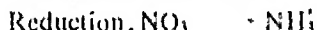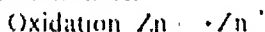
Oxidation: $6 \times (Fe^{2+} \longrightarrow Fe^{3+} + e)$

Reduction: $1 \times (6e + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O)$

Adding: $6e + 6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 6e$

The final balanced equation is:

$$6Fe^{2+} + 14H^+ + Cr_2O_7 \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Example 10.2

Balance the following equation in a basic solution :

$$NO_3 + Zn \longrightarrow Zn^{2+} + NH_3$$

Solution

Let us do this problem in short.

Oxidation $Zn \longrightarrow Zn^{2+}$

Reduction. $NO_3 \longrightarrow NH_3$

1.   First take the oxidation half equation

(a) balance all atoms other than H and O, already done

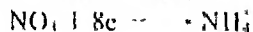(b) Add electrons to make up for the difference in oxidation number

$$Zn \longrightarrow Zn^{2+} + 2e$$

(c) Balance the charges: already done

(step (d) is not needed)

2.   Let us take the reduction half equation

$$NO_3 \longrightarrow NH_3$$
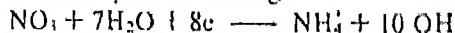
(a) Balance all the atoms other than H and O done

(b) Add electron to make up for the difference in oxidation number (N from oxidation number +5 changes to oxidation number −3 Difference of 8 electrons).
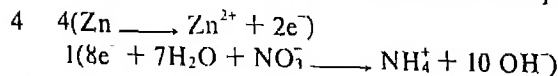
$$NO_3 + 8e \longrightarrow NH_3$$

(c) Balance the charges : In basic solution, OH ions are needed to account for extra negative charges. Total charge on left is −9, on the right it is + 1. Therefore, ten OH are needed on the right.

$$NO_3 + 8e \longrightarrow NH_3 + 10 OH$$

(d) Add water molecules to complete balancing.

$$NO_3 + 7H_2O + 8e \longrightarrow NH_3 + 10 OH$$
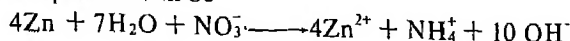
3   Check that the half equations are balanced both in mass and charge and that electrons appear on opposite sides of the two equations

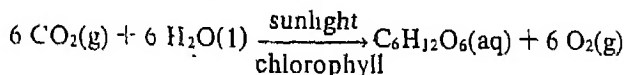4 $4(Zn \longrightarrow Zn^{2+} + 2e^-)$
    $1(8e^- + 7H_2O + NO_3^- \longrightarrow NH_4^+ + 10\ OH^-)$

Adding
$$4Zn + 8e^- + 7H_2O + NO_3^- \longrightarrow 4Zn^{2+} + NH_4^+ + 10\ OH^- + 8e^-$$
The final balanced equation will be·
$$4Zn + 7H_2O + NO_3^- \longrightarrow 4Zn^{2+} + NH_4^+ + 10\ OH^-$$

Oxidation-reduction reactions are the basis of many applications of chemistry in human activity. Some examples are·

(i) Metal oxides are reduced to metals by using suitable reducing agents. Fe_2O_3 is reduced to iron in a blast furnace using coke Al_2O_3 is reduced to aluminium by cathodic reduction in an electrolytic cell

(ii) Electrical energy demand in a space capsule is met out of reaction between hydrogen and oxygen used in fuel cells, which are electrochemical cells with hydrogen and oxygen electrodes.

(iii) Photosynthesis is an important process through which green plants convert carbon dioxide and water into carbohydrate in the presence of light.

$$6\ CO_2(g) + 6\ H_2O(l) \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6(aq) + 6\ O_2(g)$$

Here CO_2 is reduced to a carbohydrate and water is oxidised to oxygen, with light providing the energy required for this reaction.

(iv) Oxidation of fuels is the most important source of energy that meets our daily needs

Fuels (wood, gas, kerosene, petrol) $+ O_2 \longrightarrow CO_2 + H_2O +$ other products $+$ energy.
In living cells, glucose, $C_6H_{12}O_6$ is oxidised to CO_2 and water in the presence of oxygen and energy is released:

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O\ (l) + energy.$$
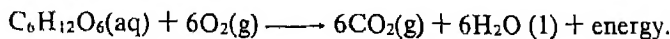
EXERCISES

10.1   Write the following redox reactions using half equations.
(i) $Zn(s) + PbCl_2(aq) \longrightarrow Pb(s) + ZnCl_2(aq)$
(ii) $2\ Fe^{3+}(aq) + 2\ I^-(aq) \longrightarrow I_2(aq) + 2Fe^{3+}(aq)$
(iii) $2Na(s) + Cl_2(g) \longrightarrow 2NaCl\ (s)$
(iv) $Mg\ (s) + Cl_2(g) \longrightarrow MgCl_2(s)$
(v) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

10 2   In the reactions given in the above question mention
        (i) Which reactant is oxidised? To what?
        (ii) Which reactant is the oxidiser?
        (iii) Which reactant is reduced? To what?
        (iv) Which reactant is the reducer?

10 3   Write correctly balanced equations for the following redox reactions using half
        reactions:
        (i) $H_2S + Fe^{1+} \longrightarrow Fe^{2+} + S + H^+$
        (ii) $I + IO_3^- + H^+ \longrightarrow I_2 + H_2O$
        (iii) $Bi(s) + NO_3 + H^+ \longrightarrow NO_2 + Bi^{1+} + H_2O$
        (iv) $I^- + O_2(g) + H_2O \longrightarrow I_2 + OH$
        (v) $Cu(s) + Au^+ \longrightarrow Au(s) + Cu^{2+}$

10 4   In question 10 3 state what is oxidised to what and what is reduced to what in the
        reactions expressed by the equations.

10 5   Consider the following reactions that produce electricity in a galvanic cell
        (i) $2Fe^{3+} + 2 Cl^- \longrightarrow 2Fe^{2+} + Cl_2 (g)$
        (ii) $Cd(s) + I_2 \longrightarrow Cd^{2+} + 2 I$
        (iii) $2Cr(s) + 3Cu^{2+} \longrightarrow 3 Cu (s) + 2 Cr^{3+}$
        Write the anode and cathode reactions for the galvanic cell. Specify the nature of the
        anodes and cathodes. Write the cell in the usual notation.

10.6   The charge of an electron is 1.60219×10^{19} coulomb. Calculate the value of the
        Faraday constant, F
        (Hint: one mole electron is one Faraday)

10.7   Write the anode reaction, the cathode reaction, and the net cell reaction for the
        following cells Which electrode would be the positive terminal in each cell?
        (i) $Zn (s) / Zn^{2+} // Br , Br_2 / Pt (s)$
        (ii) $Cr (s) / Cr^{3+} // I^-, I_2 / Pt (s)$
        (iii) $Pt (s) / H_2 (g) / H^+ (aq) // Cu^{2+} /Cu (s)$

10.8   Calculate the EMF of the cells formed by various combinations of the following
        standard half cells. Here, since we are considering standard cells $[M^{n+}] = 1$ mol l. ')

        (i) $Zn(s)/Zn^{2+} (aq)$ (iv) $Ni(s)/Ni^{2+} (aq)$
        (ii) $Cr(s)/Cr^{3+} (aq)$ (v) $Co(s)/Co^{2+} (aq)$
        (iii) $Cu(s)/Cu^{2+} (aq)$ (vi) $Ag(s)/Ag^+ (aq)$
        Also calculate the standard potentials of such cells.

10.9   Calculate the EMF of the cell
        $Pb (s)/Pb(NO_3)_2 (M_1) // HCl (M_2)/H_2(g)/Pt(s)$ when
        (i) $M_1 = 0.100M, M_2 = 0.200 M$; and $P_{H2} = 1.00$ atm
        (ii) $M_1 = 1.050 M, M_2 = 1.00 M$, and $P_{H2} = 1.00$ atm
        (iii) $M_1 = 1.00 M, M_2 = 0.40 M$, and $P_{H2} = 1.00$ atm

10 10 With the help of Table 10 1, select an oxidising agent capable of transferring
(i) Cl^- to Cl_2 (ii) I^- to I_2
(iii) Pb to Pb^{2+} (iv) Fe^{2+} to Fe^{3+}
and also select a reducing agent that can convert
(i) Fe^{2+} to Fe (ii) Ag^+ to Ag (iii) Al^{3+} to Al

10 11 The observed EMF of the cell
Pt (s)/H_2 (g) 1 atm/H^+ ($3 \times 10^{-4}M$) // $H^+(M_1)$/H_2 (g, 1 atm)
Pt(s) is 0 154. Calculate the value of M_1 (This problem illustrates a most commonly used method for determining the pH of a solution).

10.12 Calculate the oxidation number of all the atoms in the following compounds and ions $PbSO_4$, BrF_3, CrO_4^{2-}, MnO_4^-, CH_4, Sb_2O_5, $(NH_4)_2SO_4$, $C_6H_{12}O_6$

10.13 Balance the following redox reactions·
(i) Copper reacts with nitric acid A brown gas is formed and the solution turns blue $Cu + NO_3^- \longrightarrow NO_2 + Cu^{2+}$
(ii) $Cr(OH)_4^- + H_2O_2 \longrightarrow CrO_4^{2-} + H_2O$ (basic solution)
(iii) $SnO_2 + C \longrightarrow Sn + CO$
(iv) $Fe_2O_3 + C \longrightarrow Fe + CO$

10.14 Write correctly balanced half reactions and the overall equations for the following skeletal equations. Also find out the change in the oxidation numbers of the underlined atoms·
(i) $\underline{NO_3^-} + \underline{Bi} (S) \longrightarrow \underline{Bi}^{3+} + \underline{NO_2}$ in acid solution
(ii) $\underline{Fe} (OH)_2(s) + H_2O_2 \longrightarrow \underline{Fe}(OH)_3(s) + H_2O$ in basic solution
(iii) $\underline{Cr_2O_7^{2-}} + C_2H_4O^- \longrightarrow C_2H_4O_2 + \underline{Cr}^{3+}$ in acid solution
(iv) $\underline{MnO_4^-} + H_2C_2O_4 \longrightarrow \underline{Mn}^{2+} + CO_2$ in acid solution
(v) Al(s) + $\underline{NO_3^-} \longrightarrow \underline{Al} (OH)_4^- + NH_3$ in basic solution
(vi) $Cr_2O_7^- + Fe^{2+} \longrightarrow \underline{Fe}^{3+} + \underline{Cr}^{2+}$ in acid solution
(vii) $\underline{MnO_4^-} + Br^- \longrightarrow \underline{Mn}^{2+} + \underline{Br_2}$ in acid solution
(viii) $\underline{PbO_2} + Cl^- \longrightarrow \underline{ClO}^- + \underline{Pb} (OH)_3^-$ in basic solution

10.15 Starting with the correctly balanced half reactions write the overall net ionic reaction in the following changes
(i) Chloride ion is oxidised to Cl_2 by $\underline{MnO_4^-}$ in acid solution
(ii) Nitrous acid ($H\underline{N}O_2$) reduces $Mn\underline{O_4^-}$ in acid solution
(iii) Nitrous acid ($H\underline{N}O_2$) oxidises $\underline{I}^-$ to I_2 in acid solution
(iv) Chlorate ion ($Cl\underline{O_3^-}$) oxidises Mn^{2+} to $MnO_2(s)$ in acid solution
(v) Chromite ion ($\underline{Cr}O_3^-$) is oxidised by H_2O_2 in strongly basic solution
Also find out the change in the oxidation numbers of the underlined atoms.